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REVISION OF THE ATOMIC WEIGHT OF ALUMINUM.

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[Continued from p. 20.]

Second Series of Experiments.

Preparation and purification of Aluminum Bromide.—Aluminum bromide was prepared by the action of liquid bromine upon metallic aluminum of commerce, and was afterwards carefully purified. The first action is so violent that without special precaution the process involves some danger. In a first attempt a lump of aluminum weighing 15 to 20 grams was dropped into a long-necked flask containing a considerable quantity of bromine. There was little action for a few moments, but as soon as it began vivid combustion took place, torrents of bromine vapor were driven forth, and after the flask had cooled the surplus metal was found to have been completely fused and had nearly melted its way through the glass.

By the following arrangement the bromide was prepared in large quantity and without any trouble. About 50 cc. of bromine was placed in a large untubulated retort of hard Bohemian glass, the neck of the vessel standing vertically upwards, and an elongated

piece of ingot aluminum, the upper end of which was firmly tied with aluminum wire to a glass rod, was cautiously dipped into the liquid and withdrawn as soon as violent action began. By alternately lowering and raising the glass rod the lower end of the metal was immersed in the bromine at intervals short enough to keep up the temperature of the latter and make the action practically continuous, while there was no actual ignition, and but little bromine vapor was lost. As soon as a considerable portion of this bromine had become converted into aluminum bromide the further action became manageable. The remainder of the main quantity of metal to be treated was now at once added in lumps of 10 to 20 grams each; a long tube funnel with a glass stop-cock near the upper end was introduced into the neck of the retort, and liquid bromine was allowed to drip in at just such a rate as to keep up steady but not inconveniently violent action, taking care to keep the metal always covered. When the pieces of metal had nearly disappeared the supply of bromine was stopped, about 30 grams more of aluminum was added in filings, the contents of the retort were digested for 4 hours at about 230°C ., and the fluid portion was then decanted off from the insoluble residue into another (tubulated) retort. Most of the silicon was left undissolved as a brown amorphous powder. Most of the iron was converted into ferric bromide, which, during the continued heating, was in part broken up, leaving ferrous bromide instead. A little copper derived from one sample only of the aluminum used, was of course converted into bromide also.

More than a kilogramme of crude aluminum bromide being thus prepared, it was purified by repeated fractional distillations at carefully regulated temperature, using as a receiver in each case the retort to be next employed, and adding each time, except the last, a few grams of aluminum filings. About a sixth of the whole amount was each time first distilled off and rejected as liable to contain silicon bromide, a little of this compound actually occurring in the earlier distillations; and another sixth was left behind, in order to retain the iron, which was separated with greater difficulty. After five distillations the bromide was obtained perfectly colorless, and boiling steadily at 263.3°C . under 747 mm. pressure. Specimens were dissolved in water, and carefully examined for iron, silicon, copper, and other conceivable impurities, but none could be found. As an additional precaution, the last distillation was

effected in a slow stream of pure nitrogen, so as to avoid any formation of oxide or oxybromide of aluminum, the propriety of this being suggested by Berthelot's recent results¹ as to the thermic relations of aluminum to oxygen and the haloids, and the distillate was collected in three successive portions, the results of whose analysis will be separately given further on; they go to show that these three portions were sensibly identical. The individual specimens of pure bromide required were collected in little tubes of thin, hard glass, previously closed in at one end, carefully dried, and sealed at the other as soon as the tube was nearly filled, the fused bromide having been introduced through a miniature tube funnel to avoid smearing the upper end of the collecting tube, and a new, perfectly dry funnel used each time. The weight of each collecting tube had been taken beforehand, and the piece of glass drawn off in sealing being washed, dried, and weighed, the weight of the sealed tube itself was known, the difference between this and the total weight of tube and contents giving the amount of bromide.

Experiments to determine the amount of bromine in this compound by precipitation with a silver solution have the advantage over those of Dumas, above quoted, upon the chloride that, as Stas has shown,² silver bromide practically does not share with the chloride of this metal the slight solubility in the exactly neutralized liquid from which precipitation has been effected which renders difficult an exact determination of the amount of silver needed. Pursuing in general the course so carefully examined by Stas, the following were the details of the method employed.

Preparation of pure metallic silver.—Pure metallic silver was prepared by dissolving in nitric acid nearly pure silver already on hand, diluting largely, precipitating with pure hydrochloric acid, digesting the precipitate with aqua regia, washing thoroughly, and reducing the purified chloride in the liquid way with sodium hydrate (from metallic sodium) and invert-sugar (from perfectly pure and well crystallized cane-sugar boiled with dilute hydrochloric acid). The metal, after having been carefully tested, was fused by a jet of purified hydrogen mixed with rather less oxygen than necessary for perfect combustion. To avoid the necessity for any cutting up afterwards with steel tools, the pulverulent metal was

¹ Bulletin de la Société Chimique de Paris, 20 Mars, 1879, 263.

² Comptes rendus, 73, 998. Annales de Chimie et de Physique [5], 3, 289.

divided into a number of little lots of various weight, and these were supported upon the surface of little blocks made by compressing pure sugar charcoal (from cane-sugar quite free from heavy metals) made into a paste with pure cane-sugar syrup and gradually drying and heating to redness.¹ The fused silver thus obtained was examined for occluded oxygen, following the method of Dumas² in his recent experiments. It was supported upon a thin layer of pure lime in a hard glass tube, and heated to moderate redness in a Sprengel vacuum. The amount of oxygen given off was less than that obtained by Dumas, doubtless owing to the fact that his silver was fused under nitre and borax, while mine was, as just stated, melted on a surface of carbon with no flux. He obtained at the rate of 57 cc. of oxygen (for 0° C. and 760 mm.) per kilogramme of silver, and in other experiments, prolonging notably the time of fusion, as much as 158 cc. and 174 cc. I obtained but 34.63 cc. per kilogramme, and in another experiment made by Mr. Santos, then a student in this Laboratory, the silver having been fused upon ordinary wood charcoal, but 30.12 cc. was given off. All the silver used in the atomic weight determinations was, in separate portions, heated in the Sprengel vacuum as long as any gas was expelled, and, having been treated with pure hydrochloric acid to remove any possibly adhering particles of lime, the granules were finally washed with pure water, dried, and kept for use in a glass stoppered bottle. An approximate calculation having been made of the quantity of silver which would be required to precipitate each of the specimens of aluminum bromide, an amount less than this by something under a decigramme was dissolved in nitric acid in a strong flask closed with a stopper, which was carefully opened when cold, and the contents were somewhat further diluted with water. The amount of specially purified nitric acid used was apportioned so as to leave the smallest possible excess after solution of the metal.

Precipitation of silver bromide.—Details of method used.—To avoid the danger of losing aluminum bromide when it was brought in contact with water, the action being quite violent and attended with dispersion of white fumes, each one of the sealed thin glass tubes containing the bromide was, when the time came for using

¹ This form of support had the advantage that if any particles of carbon should be mechanically enclosed in the silver they would be readily seen on solution of the latter in nitric acid.

² Comptes rendus, 86, 65. Chem. Centralblatt, 27 Febr. 1878, 138.

it, cautiously marked with transverse scratches at intervals of about half-an-inch by means of a writing diamond, and a strong glass bottle with a very well ground stopper having had a sufficient quantity of pure water placed at the bottom, the tube was broken across at the uppermost scratch, above the surface of the bromide, the empty point was dropped into the bottle, and the rest of the tube carefully lowered by means of a loose fitting spiral of platinum wire held sideways, so as to rest by the closed end on the bottom of the bottle without allowing the water to reach the bromide until the stopper had been inserted and tied down. By now gently inclining the bottle the water was brought very gradually into contact with the aluminum bromide, without dangerously violent action and without possibility of loss.

As soon as solution was complete and the bottle had cooled down the stopper was removed, any liquid adhering to it washed back into the bottle, and a stout glass rod with square end was used to gently crush the tube to small fragments, as otherwise its contents could not have been brought fairly into contact with the silver solution, since the interior of the tube would have become plugged up with silver bromide. The scratches previously made upon the glass rendered it easy to break it up without any splashing, and the rod was then well washed with pure water allowed to run directly into the bottle. The silver nitrate solution destined for this particular specimen was now washed out of the flask in which it had been shortly before prepared into the bottle containing the bromide, the stopper was again inserted, and the bottle was vigorously shaken as in the usual Gay-Lussac silver assay. The precipitation of the bromine was completed with a very carefully adjusted solution of silver nitrate, containing 1 milligramme of silver per cubic centimetre, and delivered from a burette¹ reading clearly to $\frac{1}{10}$ th cc. The correspondence in capacity of the burette and measuring flask used was well ascertained. It was at first intended to use, for some at least of the experiments, an excess of silver, filter off the silver bromide formed, and determine silver in the filtrate by Volhard's method² with a standard solution of sulpho-cyanate; but this plan was abandoned as less simple, and probably requiring further investigation in regard to inherent

¹ This burette was simply drawn down to proper bore at the bottom, and the flow of the liquid was regulated by the admission of air through a well ground stop-cock at the top.

² Fresenius' Zeitschrift für analyt. Chemie, 18ter Jahrg., 2tes u. 3tes Heft., S. 271.

sources of error and limits of accuracy. The completion of the reaction was therefore ascertained simply by very cautious addition of the standard silver solution until all trace of turbidity ceased, verifying the result by counter test with a drop of very dilute solution of potassium bromide. By letting the bottle stand for a little while after each addition of silver solution and shaking, and then tilting it to one side so as to bring the upper portion of the liquid above the line it had before occupied on the glass, letting the new drop fall gently in, an exceedingly slight cloud was easily seen.

It should be added that the silver globules and the tubes of aluminum bromide, after final cleansing and drying, were handled only with forceps, so as to avoid any risk of traces of chlorides being taken up from the fingers, and due attention was given to the freedom of the laboratory atmosphere from hydrochloric acid or chlorine in other volatile forms.

Direct results of second series of experiments.—The results of the experiments made in this way were—

A.—Aluminum bromide from first portion of last distillate.

I.—	6.0024	grams of AlBr_3 required	7.2793	grams of Ag for precipitation.
II.—	8.6492	" "	10.4897	" "
III.—	3.1808	" "	3.8573	" "

B.—Aluminum bromide from second portion of last distillate.

IV.—	6.9617	grams of AlBr_3 required	8.4429	grams of Ag for precipitation.
V.—	11.2041	" "	13.5897	" "
VI.—	3.7621	" "	4.5624	" "
VII.—	5.2842	" "	6.4085	" "
VIII.—	9.7338	" "	11.8047	" "

C.—Aluminum bromide from third portion of last distillate.

IX.—	9.3515	grams of AlBr_3 required	11.3424	grams of Ag for precipitation.
X.—	4.4426	" "	5.3877	" "
XI.—	5.2750	" "	6.3975	" "

Third Series of Experiments.

Preparation of pure metallic aluminum.—A further supply of pure aluminum bromide having been made as above described, it was used to prepare metallic aluminum by reduction with sodium.

With a view to render the bromide more manageable while in contact with the air, it was decided to unite it with an alkaline chloride, as the aluminum and sodium chloride is used in the ordinary process of Deville, and in order to keep down the melting point, a mixture of both potassium and sodium chlorides was employed. The two alkaline salts were separately purified, carefully tested, well dried in platinum vessels, mixed in the proportion of one molecule of each, the mixture fused in lots of about 250 grams in a platinum dish over a gas furnace, poured out into another such dish standing on a block of cold iron, the thin cake gently crushed to a coarse powder while still warm in a mortar of hard glazed porcelain (from which, it was afterwards proved by examination, no silica was taken up), and the pulverized product kept until needed in a well stoppered bottle. Separate portions of the purified aluminum bromide having been in the last distillation collected in tared glass flasks and weighed, a quantity of the above mixture of alkaline chlorides was weighed off for each corresponding to 1 molecule $(K+Na)Cl$ for 1 molecule $AlBr_3$, and the flask having been heated until the bromide was fused, the potassio-sodic chloride was cautiously added. Very marked rise of temperature occurred, so that in a first attempt, using considerable quantities of the materials and mixing them abruptly, since such an effect had not been foreseen, the flask was violently cracked, and torrents of aluminum bromide vapor were driven off. This evolution of heat is interesting as evidence of chemical combination taking place, not only between two chlorides or two bromides, but between a chloride and a bromide. The fused mass was on cooling crushed to small fragments and coarse powder and preserved in a well-stoppered bottle. The precaution was not omitted of testing for any evidence of impurity derived from the flasks or mortar, but with negative result. The material thus prepared did not fume in the air, was sufficiently slow in taking up atmospheric moisture to be managed without difficulty, and fused on re-heating to about $130^{\circ}C$. The sodium to be used in decomposing it was in large ingots, which when needed were wiped to remove naphtha, the outer crust cut off with a knife, the large pieces roughly weighed, and the proper quantity rapidly cut up into small fragments without again moistening with naphtha.

The great difficulty in the way of obtaining pure metallic aluminum consists in obtaining crucibles of suitable material, especially

such as shall not yield either iron or silicon. M. Tissier¹ seems to have been more fortunate than I in the use of carbon vessels. The crucibles of hard carbon which I had on hand, purchased in Germany, contained both the above-named impurities, which were taken up in no small quantity by the aluminum; and I failed in sundry attempts to make crucibles of purer carbon, or to use this substance as a lining, the carbon either burning away, crumbling up, or permitting the fused materials to pass through its pores or through cracks in the mass. I at last succeeded in adapting to my purpose alumina itself, sufficiently cemented together by sodium aluminate. I was indebted to Henry Pemberton, Esq., Vice President of the Pennsylvania Salt Manufacturing Company at Natrona, Pennsylvania, and to W. N. Richard, Esq., of the same works, for an abundant supply of aluminum hydrate, such as is thrown down by a stream of carbon dioxide from solution of sodium aluminate in the process of making soda from cryolite. This was not absolutely free from iron, but one lot contained traces only of this metal, insufficient, as it turned out, to contaminate the aluminum to be made in contact with it. The hydrate was strongly heated in well covered crucibles until it ceased to give off water; the alumina which was left required then to be guarded from the air, as it readily took up moisture again. All attempts to use it mixed with water and any unobjectionable cementing material to a plastic mass failed from excessive shrinkage and crumbling, but by mixing it in the dry state with dry sodium aluminate better results were obtained. The sodium aluminate had to be specially prepared, as that made (for soap-boilers' use) at Natrona from cryolite contained too much iron. The dry mixture was pressed into wooden moulds, and three or four crucibles thus made having been very slowly and cautiously heated up in a gas furnace, stood fairly the necessary temperature of the reduction of aluminum, although they were very fragile. On the whole, however, it was found best to use a highly aluminous Beaufaye crucible, with a thick lining of this mixture of dry alumina and sodium aluminate well rammed in and very gradually heated. There were some failures from cracking of the crucibles or linings, and whenever the slightest contact of the metallic aluminum with the outer crucible occurred, silicon and generally iron were sure to be found in the metal. With successful prevention of this by an adequately thick and perfectly continuous lining

¹ Comptes rendus, *loc. cit.*

there was much difficulty in securing a sufficiently high temperature in the interior, since the conducting power for heat of the alumina linings seemed to be quite low. This led to much loss of sodium by combustion, and but a very small yield indeed of really pure aluminum was secured. When the crucible had been heated up ready for the reduction, a small quantity of the pulverized mixture of potassium and sodium chlorides was thrown in; soon afterwards the aluminum bromide (which had been fused with the alkaline chlorides) with the proper quantity of sodium was introduced,¹ and as soon as the violent reaction was over a further portion of the mixed alkaline chlorides.

Only the large, well-fused globules of aluminum were picked out; these were re-fused once or twice before a blowpipe flame upon a support of alumina, to free them from any possible remains of the flux; any trace of oxide was detached by acting slightly upon the surface with pure hydrochloric acid, and the globules were then well washed with water, and dried by a gentle heat. Specimens cut from different portions of the globules were carefully tested, particularly for silicon, iron, sodium, and potassium; and a sufficient quantity of the metal for the intended experiments was found to yield no appreciable trace of impurity. The surface of the specimens to be used which had touched the cutting pliers was again cleansed by acid and water. This pure aluminum did not differ much in physical character from the ordinary metal of commerce: it seemed, however, to be somewhat whiter, was distinctly softer, and had a little higher density, the mean of three closely agreeing determinations made at 4° C. giving the number 2.583 as referred to water at the same temperature.

Production of hydrogen by aluminum, and measurement of the gas.—Details of method used.—The pure metal was used for the determination of its atomic weight by acting upon a known weight of it with a strong solution of sodium hydrate and determining the amount of hydrogen evolved. The advantage of using an alkali rather than hydrochloric acid, as in Terreil's experiment above quoted, lies in the non-volatility of the former, only vapor of water having to be separated from the hydrogen, while sulphuric acid is

¹ Aside from the question of expense there is some advantage in using aluminum bromide for making the metal, on account of the low melting-point of the sodium bromide which is left. Carnelley's recent determinations (Chem. Soc. Journ., July, 1878, pp. 279, 280) make the melting-point of sodium bromide 708° C., while that of the chloride is 772°, and that of the fluoride above 902°.

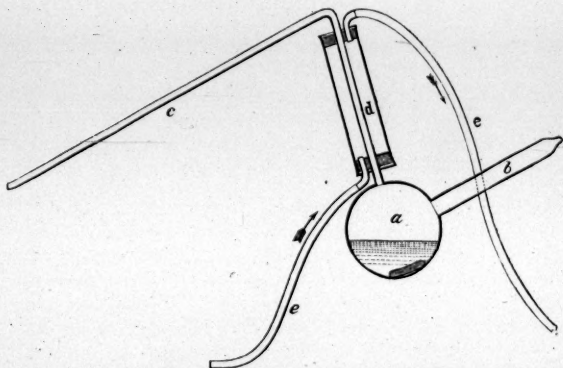
not available on account of the resistance to its action of aluminum. In 1863 Fr. Schultze¹ proposed to measure the volume of hydrogen given off by the action of an alkaline solution on commercial aluminum as the means of approximately deciding on the comparative purity of different specimens. The nature of the reaction was established by preliminary experiments, which proved to me that normal sodium aluminate alone is formed, so that each atom of aluminum liberates three atoms of hydrogen. The sodium hydrate was prepared from metallic sodium, and was used in the form of a solution so strong as scarcely to lose a sensible amount of water by the passage through it of a dry gas at common temperature—such an alkaline solution, so far as strength is concerned, as would be used to absorb carbon dioxide in an organic analysis. The quantity taken for each experiment was but a few cubic centimetres, and but little beyond the exact amount required for the solution of the metal; a small excess was, however, always allowed, so that the action might not become very languid towards the end. This strong alkaline solution was prepared with water which had been boiled to expel air, and the solubility in it of hydrogen was ascertained to be so small that any correction on this account would have fallen within the limits of inevitable error, and might be safely neglected.

To secure accurate measurement of a somewhat large volume of hydrogen, two stout flasks were selected, one holding about a litre and the other about half as much, and with narrow necks of rather more than usual length; and on the necks a simple millimetre scale was marked. One of these flasks having been carefully filled with mercury and inverted over the mercurial trough, the hydrogen was collected in it, such a quantity of aluminum being used in each experiment as previous trials had shown would yield gas enough to bring the level of the mercury within the range of the scale on the neck. To thus obtain such a volume of gas as could be accurately measured in the narrow part of the flask it was necessary to note in advance roughly the prevailing temperature and pressure, and to take advantage of a time when these were not undergoing much change. The level of the mercury having been noted on the millimetre scale, the corresponding volume was afterwards determined by calibration with mercury, weighed in portions of about half a kilogramme.

¹ Fr. Schultze, "Die gasvolumetrische Analyse," S. 18, quoted in v. Wagner, Jahresbericht, u. s. w., 1864, S. 23.

The little piece of apparatus used for the solution of the aluminum is shown in fig. 2, in which (*a*) represents a glass bulb of about 65 mm. diameter; (*b*) a tube connected therewith, originally open at both ends, and about 12 mm. diameter and 175 mm. long, but afterwards reduced in length to about 100 mm. by drawing off and sealing, as shown in the figure; (*c*) is the much smaller tube for carrying off the gas produced; (*d*) is a water jacket like that of the common Liebig's condenser, formed by a piece of larger tube surrounding the ascending limb of (*c*), and put in place before (*c*) was bent; while (*e, e*) represent small india-rubber tubes for circulating a current of water through (*d*).

Fig. 2



Each experiment was made as follows: The proper quantity of strong solution of sodium hydrate, its volume accurately measured, having been introduced into the bulb by means of a little tube funnel passed through (*b*), taking care to leave the surface of the latter clean, the aluminum (usually in a single piece of elongated shape) was passed into (*b*), held nearly horizontal, so that the metal did not slip down into the bulb, but rested 40 or 50 mm. from it. (*b*) was now drawn off and sealed with a well-rounded end. The bulb was touched for a moment or two with the hand, so as to expel a very little air, and the outer end of the small tube (*c*) was introduced into the mercury of the trough, taking care that

(*b*) was still kept in such a position as to prevent the aluminum coming in contact with the alkaline solution. After a sufficient lapse of time for the apparatus to have acquired the temperature of the room, the barometer and thermometer and the difference of level of the mercury in the trough and in (*c*) were read off¹; so that, knowing the volume of alkaline solution introduced and of aluminum (the latter from its weight), calibration of the bulb and tubes after the experiment was over completed the data necessary to determine the volume of air which the apparatus contained at the beginning. The aluminum was now made to slide down into the bulb, the end of the gas-delivery tube (*c*) having been brought under the mouth of the measuring flask. Over-rapid evolution of hydrogen and any considerable rise of temperature were prevented, partly by tilting the bulb so that the little piece of aluminum rested against one side and exposed but a part of its surface to the action of the liquid, and partly by cooling the outside of the bulb with water; while, on the other hand, it sometimes became necessary to gently warm the liquid towards the end of the experiment. To guard against more than traces of aqueous vapor being carried away with the hydrogen, a current of ice-water was kept up through (*d*). As soon as the last of the aluminum had disappeared, leaving the liquid quite clear, (*c*) was brought up into a nearly vertical position, and the apparatus left to itself until the temperature of the room had been attained. The barometer and thermometer, height of mercury in (*c*) above that in trough, and level of mercury in neck of measuring flask (after the last traces of moisture had been removed from the hydrogen by means of a stick of caustic potash), with its height above that in trough, were now read and recorded. Lifting (*c*) straight up from the trough, the mercury in this tube was got out by running a wire up and down in it, and inverting it, the whole of the remaining space in (*a*), (*b*), and (*c*) was filled up with alkaline lye of the same strength with that already contained, this liquid being run in from a graduated burette through a slender tube funnel, and the volume used noted, so as to show how much liquid had been already present. The apparatus being now emptied, washed out, and calibrated (with water, instead of mercury, on account of the difficulty of getting the interior quite dry), the volume of gas remaining in it at the close of the experiment was had from the difference between the total capacity (to the level of the

¹ All readings were of course made from a distance with the aid of a small telescope.

mercury in (c)) and the volume of liquid which the bulb had contained at the close of the experiment, these taken together with the data for pressure and temperature.

On account of slight rise of temperature during the solution of the metal, the volume of hydrogen left in the bulb and tubes was always less than the air in the same at the beginning; and, after reduction to normal temperature and pressure, the difference had to be subtracted from the volume of gas collected in the flask.

In order to connect the weight of the aluminum with the weight of the hydrogen, the latter being obtained from its observed volume and Regnault's determination of its density, it was necessary that the weight of the metal should be absolute, or in terms of equal value with those used in Regnault's researches; hence, as has been already stated, the weights used were such as had had their real value determined, and the precaution of double weighing was applied. The quantities of metal used being small, the centre of gravity of the balance beam was so adjusted as to give great sensitiveness.

In calculating the weight of the hydrogen from its volume, the difference in the value of the force of gravity at Paris and at the University of Virginia had to be taken into account. In view of the difference of latitude and elevation above the sea this constant is, in C.G.S. units,

For Paris	980.94
For University of Virginia . . .	979.95

and, applying the difference in nominally normal pressure at the two places, Regnault's value for the weight of a litre of hydrogen at 0° C. and 760 mm., .089578 gram, becomes .089488 gram.

In the experiments made in this way the only assignable cause of constant error, tending to affect in a particular direction the atomic weight deduced from them, seems to be the retention in solution of traces of hydrogen by the alkaline liquid in the bulb. The tendency of this is, of course, to make the atomic weight of aluminum appear greater than it should be, but I am satisfied that the possible extent of such error must be excessively minute, inappreciable within the limits of error of observation.

Direct results of first set of third series of experiments.—The results obtained were as follows:—

A.—Hydrogen by volume at 0° C. and 760 mm.

I.—.3697	gram of Al	gave	458.8	cc.=.04106	gram of H.
II.—.3769	" "		467.9	" =.04187	"
III.—.3620	" "		449.1	" =.04019	"
IV.—.7579	" "		941.5	" =.08425	"
V.—.7314	" "		907.9	" =.08125	"
VI.—.7541	" "		936.4	" =.08380	"

Second set of experiments of third series.—*Hydrogen collected and weighed as water.*—*Details of method used.*—As the collection and accurate measurement of larger quantities of hydrogen would be difficult from the great weight of mercury to be dealt with, while it seemed desirable to repeat these experiments with a larger amount of aluminum, an arrangement was adopted for burning the hydrogen and weighing it as water.

A bulb like that described above was used for the reaction between the aluminum and solution of sodium hydrate, another small tube (which may be designated as (*x*)) being connected, however, with the bulb, for the purpose of sweeping out air at the beginning of the combustion and the remainder of the hydrogen at the end by a current of other gas. The gas from the delivery tube (*c*) was carried through a series of four drying tubes, containing in the former two pumice stone soaked with pure sulphuric acid of full strength, and in the other two well dried asbestos and loose, woolly phosphorus pentoxide; thence it passed through a long combustion tube, filled for the first two-fifths with pure, finely granular cupric oxide, which had been recently ignited, and for two-fifths more with turnings of electrotpe copper oxidized on the surface, while the last one-fifth of its length remained at first unoccupied, to be filled later as will be described; the vapor of water being finally collected beyond this combustion tube in a single light drying tube of calcium chloride, one of sulphuric acid on pumice, and one of phosphorus pentoxide.

The whole of the apparatus having been put together, with the exception of the three final drying tubes, for which at first a single unweighed calcium chloride tube was substituted, with sodium hydrate solution in the bulb, and metallic aluminum in the tube (*b*),

a slow stream of carefully purified and well dried air was passed through from (x) for some time, while the combustion tube was heated to low redness. Having allowed it to cool down to the temperature of the room, the stream of air from (x) was replaced by one of dry nitrogen; a plug of soft copper turnings with bright unoxidized surface was introduced into the further end of the combustion tube so as to fill up the unoccupied fifth of its length, and it was again brought to and kept at a red heat. After the nitrogen had passed through at this temperature for about twenty minutes, the three drying tubes for the collection of the water to be formed, having been standing for some time in the balance case, were accurately weighed, and connected with the further end of the combustion tube, the previously used and unweighed calcium chloride tube being removed. The tube (x) having been closed, the tube (b) was now tilted so as to make the aluminum slip down into the alkaline liquid, and as in the experiments already described, the rate at which the hydrogen was evolved was controlled by inclining the bulb so as to vary the extent of surface of the metal attacked, and by cooling the outside of the bulb with water.

As soon as the metal was all dissolved, nitrogen was again introduced by (x) to sweep out the remaining hydrogen, limiting the quantity of the former gas to such an amount as was thought necessary for this purpose. This nitrogen was then in turn replaced by pure and dry air, which was passed through the apparatus until the surface of the copper which had been reduced was re-oxidized, this being done to avoid any risk of occluded hydrogen being retained, while the nitrogen had served to obviate the danger of explosion. The drying tubes were then finally removed from the further end of the combustion tube, and weighed after exposure to the atmosphere of the balance case long enough to permit the surface of the glass attaining a constant condition. In both weighings the reduction to equivalent weights *in vacuo* was duly attended to, the weights and densities of all the materials making up the drying tubes and their contents having been previously ascertained. The last tube of the set was weighed separately, as was the last of the drying tubes connected with the reaction bulb, and it was found that, there being no increase of weight on the part of either of them, the absorption of aqueous vapor was sensibly complete.

Although all the precautions I could think of were taken in these experiments, the well known difficulty of absolutely excluding moisture, of which every joint to the apparatus becomes a possible source, so that in ordinary organic analysis the amount of hydrogen found may be expected to come out rather above than below the truth, leads to the suspicion that such constant error as may have been involved tended in this direction, and if so that the resulting atomic weight would be made to appear somewhat too low. The extent of error from this cause, however, if it existed at all, must have been extremely small.

Direct results of second set of experiments of third series.

The results of these last experiments were—

B.—Hydrogen weighed as water.

I.—2.1704	grams of Al	gave	2.1661	grams of H ₂ O.
II.—2.9355	"	"	2.9292	" "
III.—5.2632	"	"	5.2562	" "

Calculation of results.

In calculating the atomic weight of aluminum from the data furnished by the above described experiments, the atomic weights assumed for the other elements involved are those which result from the researches of Stas and the previous investigation by Dumas and Stas of the composition of water, namely—

$$O = 15.961$$

$$S = 31.996$$

$$N = 14.010$$

In regard to silver and bromine a difficulty arises from the fact that the relation between these elements was determined by Stas with metallic silver which, as Dumas¹ has pointed out, contained in all probability occluded oxygen. It appears from Dumas' experiments and from mine, that the quantity of oxygen which may be so retained varies with the conditions under which the metal is fused, and it is impossible now to ascertain precisely how much was present in that used by Stas, while the correction to be applied on this account, though small, is not inappreciable in its effect upon the atomic weight of the aluminum. Omitting to extract in the Sprengel vacuum the occluded oxygen from the silver used in my

¹ *Loc. cit.*

experiments would not have secured identical condition of the silver with that of the metal used by Stas, since the circumstances of fusion and cooling would probably not have been altogether the same, and it seemed best to use silver fully purified in this respect, so that my results might be directly comparable with any obtained in the future, since this source of error once pointed out ought not to be hereafter neglected. I have therefore used as the atomic weights of silver and bromine the numbers obtained by Stas (from his experiments on silver bromide and bromate), recalculated on the assumption that the metal employed by him would have yielded 57 cc. (reduced to 0° C., and 760 mm.) or 82 mgrm. of oxygen per kilogramme, this being the quantity obtained by Dumas from silver treated as nearly as possible as was in all likelihood that which Stas employed. This has the advantage of reducing the remaining error to that only which depends on the *difference* between the real amount of oxygen which was present and that assumed in such calculation, instead of leaving the whole resulting from using Stas' numbers uncorrected, my silver having had the oxygen removed, while his had not been so treated. The atomic weights adopted then for these two elements are—

$$\text{Ag} = 107.649$$

$$\text{Br} = 79.754$$

Calculated results.—The following are the values obtained for the atomic weight of aluminum from the different series of experiments, with the probable (mean) value resulting from each set, the difference from this mean of each individual experiment, and the probable error of the mean itself calculated in the usual way by the method of least squares:

First series.

A.			B.		
Experiment.		Diff. from mean.	Experiment.		Diff. from mean.
I.	Al=27.029	— .011	VI.	Al=27.114	+ .018
II.	" 27.043	+ .003	VII.	" 27.095	— .001
III.	" 27.055	+ .015	VIII.	" 27.107	+ .011
IV.	" 27.068	+ .028	IX.	" 27.067	— .029
V.	" 27.005	— .035	X.	" 27.096	.000
Mean	" 27.040		Mean	" 27.096	
Probable error of mean result $\pm .0073$			Probable error of mean result $\pm .0054$		

Second series.

A.			B.		
Experiment.		Diff. from mean.	Experiment.		Diff. from mean.
I.	Al=27.035	+ .001	IV.	Al=27.028	+ .005
II.	" 27.021	- .013	V.	" 26.993	- .030
III.	" 27.046	+ .012	VI.	" 27.036	+ .013
			VII.	" 27.028	+ .005
			VIII.	" 27.030	+ .007
Mean	" 27.034		Mean	" 27.023	
Probable error of mean result $\pm .0049$			Probable error of mean result $\pm .0052$		

C.		
Experiment.		Diff. from mean.
IX.	Al=26.999	- .019
X.	" 27.034	+ .016
XI.	" 27.021	+ .003
Mean	" 27.018	
Probable error of mean result $\pm .0069$.		

Third series.

A.			B.		
Experiment.		Diff. from mean.	Experiment.		Diff. from mean.
I.	Al=27.012	+ .007	VII.	Al=26.995	+ .005
II.	" 27.005	.000	VIII.	" 26.999	+ .009
III.	" 27.022	+ .017	IX.	" 26.977	- .013
IV.	" 26.988	- .017			
V.	" 27.006	+ .001			
VI.	" 26.996	- .009			
Mean	" 27.005		Mean	" 26.990	
Probable error of mean result $\pm .0033$			Probable error of mean result $\pm .0046$		

In view of the gradual loss of water which, as has been shown, crystallized ammonium alum undergoes on exposure to the atmosphere, I feel that of these various sets of experiments, B of the first series is entitled to least confidence, and the considerable difference between its results and the others leads me to favor its rejection. On the other hand, I am inclined to attach most weight to series 3, A, since the method used was very simple in principle, the determination of one of the two quantities concerned was

rendered very exact by the great volume occupied by the hydrogen, the comparison was made directly with the standard element in our system of atomic weights and not through the intervention of any other substance whose atomic weight must be assumed, and the agreement of the results among themselves is particularly good, as shown by the probable error of the mean being the smallest reached.

General mean of results.—The general mean from all of the thirty experiments, if all be included in the calculation, is $Al = 27.032$, with a probable error for this mean of $\pm .0045$.

If series 1, B, be excluded, the mean of all the remaining twenty-five experiments is $Al = 27.019$, with a probable error of $\pm .0030$. The third decimal having no positive value, we may take $Al = 27.02$. If integer numbers be used for O, N, C, Na, &c., $Al = 27$.

All the experiments which I have made are reported, except three or four in which there was manifest failure, as by accidental loss of material to a visible extent, and which were on that account not completed.

The general result adds, I trust, aluminum to the, unfortunately still limited, list of those elementary substances whose atomic weights have been determined within the limits of precision attainable with our present means of experiment.

Bearing of final result upon "PROUT'S law."

It is interesting to observe that this result also adds one to the cases already on record of the numbers representing carefully determined atomic weights approaching closely to integers, and leads to a word on the reconsideration of "Prout's law." The recent researches of Mr. Lockyer, not unsupported by evidence drawn from other sources, have tended to suggest the possibility, at least, that the forms of matter which as known to us under ordinary conditions we call elements may be susceptible of progressive dissociation at enormously high temperature, and, under circumstances in which this supposed state of dissociation admits of being spectroscopically observed, some of the characteristic features in the spectrum of what is usually known to us as hydrogen become in a very remarkable degree prominent. If such dissociation may really occur, and if the atoms of hydrogen as commonly

known to us form either the last term, or any term not far removed in simplicity from the last, in the progressive breaking up of other forms of matter, it is obvious that "Prout's law," or some modification of it, such as was many years ago suggested by Dumas, *must* be true, the atomic weights of all the other so-called elements must be multiples of that of hydrogen, or multiples of that fraction of the hydrogen atom which may result from the dissociation of this body itself. If such fraction be very small as compared with the effect of the inevitable errors of experiment, the experimental verification or refutation of the law will prove impossible, but if it be considerable, as for instance one-half of the commonly known hydrogen atom, or one-fourth, as assumed by Dumas, the question admits of practical examination.

Well deserved attention has for some years past been given to the labors of Stas in this direction, and his main result is no doubt properly accepted, if stated thus, that the differences between the individual determinations of each of sundry atomic weights which have been most carefully examined are distinctly less than their difference, or the difference of their mean, from the integer (or one-half or one-fourth unit) which Prout's law would require.

But the inference which Stas himself seems disposed to draw, and which is very commonly taken as the proper conclusion from his results, namely, that Prout's law is disproved, or is not supported by the facts, appears much more open to dispute.

It must be remembered that the most careful work which has been done by Stas and others only proves by the close agreement of the results that *fortuitous* errors have been reduced within narrow limits. It does not prove that all sources of *constant* error have been avoided, and indeed this never can be absolutely proved, as we never can be sure that our knowledge of the substances we are dealing with is complete. Dumas' late observations on the occlusion of oxygen by metallic silver constitute an illustration of this, some of the best of Stas' results being thereby undeniably vitiated, though probably to but a minute extent.

Of course one distinct exception to the assumed law would disprove it, if that exception were itself fully proved, but this is not the case.

As suggested by Marignac and Dumas, any one who will impartially look at the facts can hardly escape the feeling that there must be some reason for the frequent recurrence of atomic weights dif-

fering by so little from accordance with the numbers required by the supposed law.

As the question stands at present, the following 18 atomic weights are the only ones which may be fairly considered as determined with the greatest attainable precision, or a very near approach thereto, and without dispute as to the methods employed :

*Oxygen	15.961
*Nitrogen	14.010
Chlorine	35.371†
Bromine	79.757†
Iodine	126.541†
*Sulphur	31.996†
*Potassium	39.042
*Sodium	22.987
*Lithium	7.005
Silver	107.667†
Thallium	203.655‡
*Aluminum	27.019
*Carbon	11.97
*Phosphorus	30.96
Barium	136.84
Calcium	39.90
*Magnesium	23.94
Lead	206.40

If now we discard altogether Dumas' assumption of multiples of .5 or .25, and consider simply the indications afforded of Prout's law in its original form, we may safely take the first decimal place of each of these numbers as quite freed from the influence of *fortuitous* errors, while the second decimal is nearly so in many instances. It appears that out of the 18 numbers, 10 (those to which an asterisk is prefixed) approximate to integers within a range of variation less than one-tenth of a unit. What then is the degree of probability that this is purely accidental, as those hold who carry to the extreme the conclusions of Berzelius and Stas? Since there are five intervals of .1 each between any integer and the .5 which

† Stas' numbers, uncorrected for occlusion of oxygen by silver.

‡ Crookes' number modified by taking O=15.961 instead of 15.96.

divides it from the next higher (or lower) integer, the result is given by the expression—

$$5^{-18} \left\{ 1 + \frac{18}{17} \times 4 + \frac{18}{16} \times 4^2 + \frac{18}{15} \times 4^3 + \dots + \frac{18}{10} \times 4^8 \right\}$$

and the probability in question is found to be only equal to 1 : 1097.8.

Of course this result might be easily varied by assuming other limits of precision as marking accordance with the law within the range of possible constant error, but this example seems to be based upon not unfairly assumed ground in this respect, and seems sufficiently to illustrate the point that not only is Prout's law not as yet absolutely overturned, but that a heavy and apparently increasing weight of probability in its favor, or in favor of some modification of it, exists and demands consideration.

Contributions from the Chemical Laboratory of Harvard College.

X.—ON FURFUROL AND CERTAIN OF ITS DERIVATIVES.

BY HENRY B. HILL.

[Continued from p. 51.]

Dibrommaleic Acid of Kekulé.

In 1864 Kekulé¹ found among the products of the action of bromine and water upon succinic acid an acid, $C_4H_2Br_2O_4$, to which he gave the name dibrommaleic acid. It formed white, clustered needles, which were extremely soluble in water, alcohol, or ether, and melted at 112° ; at higher temperatures the acid distilled apparently unchanged, and it volatilized readily with steam. For the further characterization of the acid, Kekulé made the silver

¹ Ann. Chem. u. Pharm. 130, 1.

and lead salts. The silver salt could be precipitated from an aqueous solution of the acid, by the addition of argentic nitrate; and, according to the concentration of the solution, it appeared as a granular, crystalline precipitate, or in slender, glistening needles. The dry salt exploded violently by heat or percussion. The lead salt was thrown down by the addition of plumbic acetate to an aqueous solution of the acid, and when air-dried it was found to contain a molecule of water.

Since its discovery by Kekulé, the acid prepared in this way has been mentioned but twice, as far as I know; and these notices contain no additional facts which could serve to assist in its identification. Bourgoin¹ gives its melting point as 110° , and asserts that it distils unaltered. Fittig and Petri,² in their attempts to prepare the tribromsuccinic acid, which had been described by Bourgoin, obtained dibromsuccinic acid and a substance crystallizing in hemispherical aggregations, which, from their melting point (112°) and volatility with steam, they recognized as dibrommaleic acid.

In 1873, Limpricht and Delbrück³ described an acid of the same composition, which they made by the action of bromine and water upon mucobromic acid. They found it difficult of purification; and, in their study of it, they were to all appearance hampered by lack of material. The acid melted at $108-120^{\circ}$, and by sublimation it was converted into its anhydride, $C_4Br_2O_3$, which melted at $95-120^{\circ}$. The barium salt they obtained in colorless, tabular crystals, to which they assigned the formula, $BaC_4Br_2O_4 \cdot 2H_2O$. The silver salt they found to be insoluble; but it did not explode either by heat or percussion. They assumed, apparently without hesitation, that this acid was isomeric with that of Kekulé, and therefore named it dibromfumaric acid.

The acid made by the action of bromine upon mucobromic acid, which I have just described, agreed in most respects closely with the acid described by Kekulé; and yet the higher melting point and the ready formation of the anhydride rendered a further comparison necessary in order to settle the question of identity.

In the preparation of dibrommaleic acid, I followed in general the method of Kekulé; but, since this was to be the main product of the reaction, I was obliged to use a greater proportion of bromine and water, in order to get any considerable yield.

¹ Bul. Soc. Chim. [2] **21**, 404; **22**, 443.

² Ann. Chem. u. Pharm. **195**, 76.

³ Ann. Chem. u. Pharm. **165**, 294.

I obtained good results by using to one part of succinic acid two of water and four of bromine, and heating twenty hours at 140° . The mother liquors from which the greater part of the dibromsuccinic acid had been separated were distilled, the distillate neutralized with baric carbonate, and the baric dibrommaleate precipitated from the filtered solution. After several precipitations from aqueous solution by alcohol, it was crystallized from water by evaporation, and dried by exposure to the air. The salt could not be distinguished in outward appearance from that made from mucobromic acid.

I. 2.4931 grams of air-dried salt lost in weight, at $125-130^{\circ}$, 0.2136 gram. 0.7670 gram of this dried salt gave, on ignition with H_2SO_4 , 0.4393 gram $BaSO_4$.

II. 0.5899 gram air-dried salt gave 0.3102 gram $BaSO_4$.

Calculated for $C_4Br_2O_4Ba \cdot 2H_2O$.

Found.

		I.	II.
Ba	30.78	30.79	30.91
H_2O	8.09	8.15	

The solubility of this salt was determined according to the method of V. Meyer.

8.9841 grams of a solution saturated at 20° gave 0.2912 gram $BaSO_4$.

The aqueous solution saturated at 20° , therefore, contains 5.71 per cent. of the anhydrous salt.

From this barium salt, the free acid was made in the manner above described. In its behavior towards solvents, it resembled perfectly the acid made from mucobromic acid, and it melted between 120° and 123° . This acid I did not analyze; but the analyses published by Kekulé show too high a percentage of bromine, and in this respect do not differ essentially from those I have given above.

Calculated for $C_4H_2Br_2O_4$.

Found by Kekulé.

		I.	II.
Br	58.38	58.98	59.08

By heating this acid in a stream of carbonic dioxide, the anhydride could readily be made in appearance and behavior perfectly identical with the compound already described, and melting at $114^{\circ}-115^{\circ}$.

I. 0.4160 gram substance gave 0.2860 gram CO_2 and 0.0032 gram H_2O .

II. 0.2840 gram substance gave 0.4165 gram AgBr .

Calculated for $\text{C}_4\text{Br}_2\text{O}_3$.

C	18.75
H	...
Br	62.50

Found.

I.	II.
18.75	
C. 10.	
	62.34

The identity of the dibrommaleic acids made by the action of dry bromine upon mucobromic acid and aqueous bromine upon succinic is thus sufficiently established. They each give an anhydride melting at $114-115^\circ$; their barium salts have the same composition, $\text{BaC}_4\text{Br}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; and the solubility of these two salts in water is the same, the saturated aqueous solution containing in one case 5.66 per cent. of the anhydrous salt at 19° , in the other 5.71 per cent. at 20° .

Although I have several times tried the action of bromine and water upon mucobromic acid, according to the method of Limpricht and Delbrück, I have not as yet submitted the product obtained in this way to any very extended investigation. In all qualitative reactions it is identical with the acid I have described; and, considering the mode of its formation, one can hardly doubt its identity. Moreover, with regard to the slight differences which would seem to have induced Limpricht and Delbrück to consider their acid isomeric with Kekulé's, I have been unable to confirm their observations. The melting point ($95-120^\circ$) given by them for the anhydride does not give confidence in the purity of their material. The higher percentage of barium (31.9)¹ which they found in their barium salt would be in no way at variance with my results, even if its purity were granted, since the material they analyzed had been dried *in vacuo* (over sulphuric acid?), and my own experiments have shown that it slowly effloresces under these conditions.

Although the foregoing facts seemed to warrant the conclusion that the dibrommaleic acid of Kekulé belonged to the maleic series, inasmuch as the anhydride was the direct product of the reaction of bromine upon mucobromic acid, still I thought it advisable to

¹ Limpricht and Delbrück erroneously calculated the percentage of barium in the salt $\text{BaC}_4\text{Br}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ as 31.9 per cent. instead of 30.78, and therefore gave the same formula.

prove this directly, more especially since all analogy pointed to the formation of a derivative of fumaric acid under the conditions essential to its preparation from succinic acid. I therefore dissolved in water the pure anhydride prepared from succinic acid, neutralized the solution with baric carbonate, precipitated the barium salt by alcohol, and recrystallized it from water. This salt proved to be identical with that which was obtained directly from the acid.

0.7525 gram of the air-dried salt lost on heating to about 120° 0.0581 gram; 0.6933 gram of this dried salt gave 0.3922 gram BaSO_4 .

Calculated for $\text{BaC}_4\text{Br}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.		Found.
Ba	30.78	30.69
H_2O	8.09	7.72

The solubility was also determined by the method of V. Meyer.

7.6833 grams of the solution saturated at 19.5° gave, on evaporation with H_2SO_4 and ignition, 0.2446 gram BaSO_4 .

An aqueous solution saturated at 19.5° contained therefore 5.58 per cent. of the anhydrous salt.

This proves that dibrommaleic acid may be carried unchanged through its anhydride, and that it consequently belongs to the maleic series, unless, indeed, its behavior is radically changed by the complete replacement of its hydrogen by bromine. That such is not the case has recently been shown by Bandrowski,¹ who has discovered an acid of the same composition, which is undoubtedly dibromfumaric acid. This acid melts at $219\text{--}220^{\circ}$, and by distillation is converted into dibrommaleic acid.

Mucobromic Acid with Oxidizing Agents.

The close connection between mucobromic acid and dibrommaleic, as shown by its behavior when heated with bromine, naturally suggested the direct conversion of the one into the other by oxidation.

An aqueous solution of chromic acid does not act upon mucobromic acid at ordinary temperatures, even after standing for weeks. On warming, carbonic acid is freely given off, and at the same time a sharp, acrolein-like odor is noticed. If one atom of oxygen is employed for every molecule of mucobromic acid, a portion of the mucobromic acid seems to be completely destroyed, while nearly one-half of it remains unaltered, and may be extracted

¹ Berichte der deutsch. chem. Gesellsch. 12, 2213.

with ether after the reaction is completed. When two atoms of oxygen are taken, but little mucobromic acid escapes oxidation; but I have been unable to isolate well-marked products of the reaction, in any considerable quantities. When the solution is distilled, the substance possessing the sharp, pungent odor passes over with the steam. It is quite soluble in water, although not in all proportions, and its aqueous solution reduces silver energetically from the oxide even in the cold. Although this is the most striking product of the oxidation, it is formed in such small quantities that I have as yet been unable to study it further. After this volatile product has been distilled off, but a trace of organic acid can be extracted from the retort residue by ether. This acid is chiefly mucobromic; but with it I have found dibrommaleic acid in quantity barely sufficient for the recognition of its barium salt under the microscope when precipitated from aqueous solution by alcohol. The oxidation with nitric acid gives somewhat better results. When mucobromic acid is boiled with ten times its weight of nitric acid of sp. gr. 1.20, carbonic dioxide is slowly given off, the escaping gas renders a solution of argentic nitrate turbid, and yet, if the heat is continued for several hours, a considerable portion of the mucobromic acid is found to be converted into dibrommaleic acid. In one experiment I obtained, after several hours' boiling, from 5 grams of mucobromic acid 2.3 grams of baric dibrommaleate and 1.5 gram of unaltered mucobromic acid. This corresponds to nearly forty per cent. of the theoretical yield of dibrommaleic acid from the mucobromic acid which entered into the reaction. Stronger nitric acid oxidizes more rapidly, but the yield of dibrommaleic acid is smaller; if much more dilute acid is used, the mucobromic acid is hardly altered.

Precisely the same effect is produced by long boiling with bromine water, carbonic dioxide being evolved as before, and the yield of dibrommaleic acid remaining essentially the same. The identity of the acid made by bromine water was established by the analysis of the barium salt. This salt was precipitated several times from aqueous solution by alcohol, recrystallized from water, and contained then the required percentage of barium.

0.5493 gram of the air-dried salt gave 0.2887 gram BaSO_4 .

Calculated for $\text{BaC}_4\text{Br}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

Ba 30.78

Found.

30.90

Limpricht found that mucobromic acid was the only product when pyromucic acid suspended in water was treated with an excess of bromine at ordinary pressures. Since mucobromic acid is itself converted into dibrommaleic acid by boiling it with bromine water, it follows that the latter acid must of necessity be formed in the preparation of mucobromic acid. For its detection, the mother liquors, from which the mucobromic acid had been separated as completely as possible, were distilled. The distillate, consisting chiefly of concentrated hydrobromic acid (b. pt. 126°) was partially neutralized with potassic carbonate, and thoroughly shaken out with ether. The residue left on the evaporation of the ether was taken up with water, and the acid solution saturated with baric carbonate. Alcohol precipitated from the filtered solution baric dibrommaleate in characteristic form. For analysis, the salt was recrystallized from water, and dried by exposure to the air.

0.4709 gram of this salt gave 0.2516 gram BaSO_4 .

Calculated for $\text{BaC}_4\text{Br}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

Ba 30.78

Found.

31.41

Since the percentage of barium was found to be too high for further identification the acid was set free, and converted into the anhydride by sublimation. This crystallized in the characteristic flattened needles, which melted at 114° . The quantity of dibrommaleic acid formed in the ordinary preparation of mucobromic acid is very inconsiderable, and amounted in one case to about one per cent. of the pyromucic acid employed. The quantity must, however, of necessity be very variable.

The oxidation of mucobromic acid by means of argentic oxide was investigated by Schmelz and Beilstein. They gave to the chief product of the reaction the formula $\text{Ag}_3\text{C}_7\text{H}_2\text{Br}_3\text{O}_5$; but it is evident from an inspection of their analyses that they had in their hands the silver salt of dibrommaleic acid in a nearly pure condition.

	Calculated			Found by Schmelz and Beilstein.					
	for $\text{Ag}_3\text{C}_7\text{H}_2\text{Br}_3\text{O}_5$.	for $\text{Ag}_3\text{C}_4\text{Br}_2\text{O}_4$.	I.	II.	III.	IV.	V.	VI.	
C	11.51	9.84	10.07	10.64	11.30	...	...	...	
H	0.27	...	0.64	0.37	0.32	...	...	...	
Br	32.87	32.78	...	...	...	32.47	...	...	
Ag	44.38	44.27	...	...	...	...	44.25	44.26	

With this close agreement between the observed and calculated percentages, I did not consider it worth while to analyze, myself, this silver salt. Still it was evidently necessary to prepare from it the barium salt in order to compare this with the product I had already studied.

Since argentic bromide is readily formed when the silver salt of mucobromic acid is heated with water, I added at once an excess of argentic oxide to a warm solution of mucobromic acid, and heated it quickly to the boiling point. The oxidation seemed to be more neatly accomplished in this way than by the gradual addition of the argentic oxide, although even then there was formed a considerable quantity of argentic bromide. After the action had ceased, the whole was acidified with hydrochloric acid, and the filtered solution shaken out with ether. The acid left upon evaporation of the ether was then taken up with water, neutralized with baric carbonate, and the barium salt purified as before. An analysis of the air-dried salt, and a determination of its solubility, proved that the acid was identical with that made by the action of bromine upon succinic or mucobromic acid.

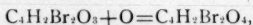
0.5225 gram of the air-dried salt gave 0.2741 gram BaSO_4 .

Calculated for $\text{BaC}_4\text{Br}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.		Found.
Ba	30.78	30.84

9.2092 grams of an aqueous solution saturated at 18.5° according to the method of V. Meyer, gave on evaporation with H_2SO_4 and ignition 0.2944 gram BaSO_4 .

According to this determination, an aqueous solution saturated at 18.5° contains 5.61 per cent. of the anhydrous salt.

This oxidation of mucobromic acid by means of argentic oxide into dibrommaleic acid,



would seem to show conclusively that it is the half aldehyde of the dibasic dibrommaleic acid.

Decomposition by Heat.

If mucobromic acid is quickly heated, the greater part of it distils unchanged; but, if the temperature is so regulated that it can distil but slowly, a great part of it suffers decomposition. The

reaction which it undergoes I have, as yet, studied only so far as to prove that dibrommaleic acid is one of the chief products. If the acid is mixed with sand and slowly distilled, streams of hydrobromic acid and carbonic dioxide are given off, and a colorless oil passes over, which, on standing, partially solidifies. On the addition of water, the solid portion dissolves, leaving an oil which is volatile with steam, and is not wholly soluble in water. Its aqueous solution reduces argentic oxide, and possesses an intolerably sharp, pungent odor. In the investigation of this oil, I have not yet obtained definite results.

The aqueous solution contained dibrommaleic acid, which was identified by an analysis of its barium salt. The solution of the barium salt obtained, at first was highly colored, and from it pure material could be made only by repeated precipitation from aqueous solution with the smallest possible quantity of alcohol. In this way, a perfectly colorless salt was made, and it was then recrystallized from water.

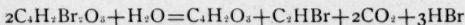
0.6652 gram of the air-dried salt gave 0.3498 gram BaSO_4 .

Calculated for $\text{BaC}_4\text{Br}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.		Found.
Ba	30.78	30.91

The amount of dibrommaleic acid thus formed is about 15 per cent. of the mucobromic acid taken, and 30 per cent. of the total weight of the distillate.

Action of Baric Hydrate.

The action of baric hydrate upon mucobromic acid was first studied by Schmelz and Beilstein. The results they obtained were extremely interesting, but needed extension in several directions. More especially inviting was the muconic acid which they considered formed in the reaction, and to which they gave the formula $\text{H}_2\text{C}_4\text{O}_3$. In beginning this investigation, Mr. O. R. Jackson and I thought it best at the outset to test experimentally the truth of the equation,



which Schmelz and Beilstein had given as an expression of the reaction, and at the same time to determine the conditions most favorable to the formation of baric muconate. The qualitative

results we found to be precisely in accordance with their statements, and it was only necessary to study the reaction quantitatively. A weighed quantity of mucobromic acid was introduced into a flask fitted with reverse cooler, and dissolved in a little warm water. The upper end of the cooler was then connected with a series of wash-bottles which were filled with an ammoniacal solution of cuprous oxide, made by reducing an ammoniacal solution of pure cupric sulphate with metallic copper. The air in the apparatus was then displaced by pure hydrogen, a measured quantity of a standard solution of baric hydrate introduced into the flask, and heat applied. When the action appeared to be finished, we determined the weight of the baric carbonate which had been formed in the reaction, the weight of the baric carbonate which could be precipitated from the filtered solution by carbonic dioxide, and the weight of the baric muconate left on evaporation after washing out the baric bromide with cold water. In order to determine the amount of bromacetylen, we filtered off the voluminous precipitate of acetylen copper which had separated in the wash-bottles, acidified the filtrate, and precipitated the bromine with argentic nitrate.

The results which we obtained are given in the following table; in each case 2 grams of mucobromic acid were taken.

No.	BaO ₂ H ₂ taken.	BaCO ₃ by CO ₂ .	Br.	BaCO ₃ formed.	" Baric muconate."
I.	1.994		0.372	0.57	
V.	2.971	trace	0.293	1.07	0.40
VI.	2.971	trace	0.333	1.05	0.55
II.	5.988	3.52	0.135	0.54	0.85
III.	5.942	3.25	0.146	0.50	0.87
IV.	5.942	3.40	0.128	0.53	0.97
VII.	8.044	5.75	0.135	0.47	0.95
VIII.	8.044	5.90	0.112	0.35	0.90

In order to compare these results more conveniently, we calculated from them the corresponding molecular ratios.

The following table contains the number of molecules of baric hydrate which we used in the various experiments for the decomposition of one molecule of mucobromic acid, the number of molecules of baric hydrate which actually entered into the reaction, and the fractions of a molecule of bromacetylen, carbonic dioxide, and baric muconate which were formed in each case. In accord-

ance with the results which we afterwards obtained, the muconate is here calculated as baric malonate.

No.	Baric hydrate.		Bromacetylen.	Carbonic dioxide.	" Baric muconate."
	taken.	used.			
I.	1.50	1.50	0.60	0.37	
V.	2.24	2.24	0.47	0.70	0.20
VI.	2.24	2.24	0.54	0.69	0.28
II.	4.51	2.21	0.22	0.35	0.43
III.	4.48	2.35	0.24	0.33	0.44
IV.	4.48	2.25	0.21	0.35	0.49
VII.	6.07	2.30	0.22	0.31	0.48
VIII.	6.07	2.17	0.18	0.23	0.45

These results were sufficient to show that, in the decomposition by baric hydrate, we had to deal with at least two independent reactions; that one of these reactions led to the formation of carbonic dioxide and bromacetylen, while the second had for its chief product the sparingly soluble barium salt—the baric muconate of Schmelz and Beilstein. Moreover, it was evident that, in order to obtain the best yield of the latter salt, a large excess of baric hydrate should be employed.

In the preparation of the sparingly soluble barium salt, we used five or six molecules of baric hydrate to one of mucobromic acid. When the reaction appeared at an end, we precipitated the excess of baric hydrate with carbonic dioxide, and evaporated the filtered solution to a small volume. When this solution was slowly evaporated upon the water bath, we found, in accordance with the statements of Schmelz and Beilstein, that the salt separated in thin crusts which had no visible crystalline structure. If, however, the solution was boiled down rapidly over the lamp, at a certain point the salt suddenly separated in fine, silky needles, which were still further increased as the solution cooled. These crystals were well washed with cold water, redissolved in boiling water, and precipitated with plumbic acetate. In this way a granular lead salt was thrown down, which, when examined under the microscope, was seen to consist of well-formed rhombic plates. For analysis, the salt was dried at 110° .

I. 0.5939 gram substance gave 0.2434 gram CO_2 and 0.0470 gram of H_2O .

II. 0.3459 gram gave, by ignition with H_2SO_4 , 0.3402 gram PbSO_4 .

	Calculated for PbC_4O_3 .	Calculated for $\text{PbC}_3\text{H}_2\text{O}_4$.	I.	Found.	II.
C	15.84	11.65	11.18		
H	...	0.65	0.88		
Pb	68.32	66.99			67.22

It will be seen that the percentages found correspond closely with those required by plumbic malonate, and differ widely from those required by the formula of Schmelz and Beilstein.

The barium salt also agrees well with the description of baric malonate given by Heintzel¹ and Finkelstein.² The analyses we have made of the salt have given us too high a percentage of barium, although materially lower than that found by Schmelz and Beilstein.

I. 0.5212 gram of the salt, dried at 120° , gave 0.5214 gram BaSO_4 .

II. 0.3455 gram of the salt, dried at 100° , gave 0.3159 gram BaSO_4 .

III. 0.2139 gram of the salt, dried at 100° , gave 0.1956 gram BaSO_4 .

	Calculated for $\text{BaC}_3\text{H}_2\text{O}_4 \cdot \text{H}_2\text{O}$.		I.	II.	Found.	III. Schmelz and Beilstein.
Ba	53.33	54.70	53.75	53.73	56.32	

The result of Schmelz and Beilstein is here calculated for the hydrous salt. They found that the salt, when dried at 100° , lost 4.15 per cent. of water at 200° , and contained then 58.6 per cent. of barium.

From the lead salt we made the free acid by means of hydric sulphide, and found it very soluble in water or alcohol, less freely in ether. From aqueous solution it crystallized in irregular rhombic plates, occasionally in more compact prismatic forms. After several recrystallizations from water, and thorough drying over sulphuric acid, these crystals melted at $131.5\text{--}132^\circ$. This agrees with the melting point of malonic acid, as given by Heintzel, although it is somewhat lower than that more recently given by Pinner.³ A combustion left no doubt of the identity and the purity of the acid.

¹Ann. Chem. u. Pharm. **129**, 133.

²Ann. Chem. u. Pharm. **133**, 343.

³Berichte der deutsch. chem. Gesellsch. **8**, 965.

0.3849 gram substance gave 0.4871 gram CO_2 and 0.1395 gram H_2O .

	Calculated for $\text{C}_3\text{H}_4\text{O}_4$.	Found.
C	34.61	34.51
H	3.85	4.03

The quantity of baric malonate which we obtained from mucobromic acid agreed with the results of our experiments upon a smaller scale, and amounted to nearly fifty per cent. of the theoretical yield. The mother liquors contained, beside baric bromide, baric formiate, whose presence could readily be established by qualitative tests.

Although the gaseous product formed by this decomposition with baric hydrate agreed closely in its qualitative reactions with bromacetylen, it seemed to us advisable to prove its identity a little more rigorously. We therefore passed the gas, diluted with hydrogen, into bromine and water. The crystalline solid which resulted we washed with dilute sodic hydrate, then with water, and finally recrystallized it from alcohol. Thus purified, it formed long, brilliant prisms, which melted at 54° . The melting point of pentabromethan is given by Lennox¹ as 48° ; by Reboul,² $48-50^\circ$; by Limpricht and Delbrück,³ $50-52^\circ$; and by Bourgoin,⁴ $56-57^\circ$. The prismatic angle could readily be determined, and the measurement of several individuals gave as its mean value $104^\circ 17'$. Reboul gives the same angle in crystals of pentabromethan as $104^\circ 20'$, and Bourgoin as $104^\circ 16'$.

The identity of the substance was still further established by analysis.

0.1151 gram substance gave 0.2547 gram AgBr.

	Calculated for C_3HBr_5 .	Found.
Br	94.12	94.17

After we had proved that malonic acid was one of the final products of the decomposition of mucobromic acid when boiled with an excess of baric hydrate, we attempted, by various modifications of the mode of decomposition, to isolate intermediate products, which might give us information concerning the nature of the reaction. After many unsuccessful experiments, we found that such products resulted from the action of alkalies at ordinary tempera-

¹ Lond. R. Soc. Proc. **11**, 257; Ann. Chem. u. Pharm. **122**, 122.

² C. R. **54**, 1229; Ann. Chem. u. Pharm. **124**, 267; Bull. Soc. Chim. 1862, 75.

³ Ann. Chem. u. Pharm. **165**, 297.

⁴ Ann. Chem. Phys. [5] **4**, 423; Bull. Soc. Chim. [2] **23**, 175, 257.

tures, and they were most conveniently studied when baric hydrate was employed.

Baric Dibromacrylate, $\text{Ba}(\text{C}_3\text{HBr}_2\text{O}_2)_2$. If mucobromic acid is gradually added to a solution of baric hydrate containing a large excess of baric hydrate in suspension, it dissolves readily, and the crystals of baric hydrate at the same time gradually disappear. After a while a beautifully crystalline barium salt begins to separate, the amount of which increases rapidly as the acid is added. In order to prepare this salt, we found it best to add the mucobromic acid until one molecule had been used for every one and a half molecules of baric hydrate. At first we used two parts of crystallized baric hydrate and four of water to one part of mucobromic acid, but subsequently we reduced the amount of water one-half. After the necessary amount of mucobromic acid had been added in small portions, care being taken to prevent any elevation of temperature, the whole was allowed to stand for a short time, and the crystals which had separated were then filtered off on the pump. These were washed with a little cold water, exposed to carbonic dioxide until neutral in their reaction, and then recrystallized from water or diluted alcohol. From alcohol, the salt crystallized in pearly rhombic plates; from water, in irregular leafy forms, or, on slow evaporation, in massive aggregates of rhombic plates. When dried by exposure to the air, they lost nothing over sulphuric acid or when heated to 80° . At 100° they slowly lost in weight.

The air-dried salt gave on analysis the percentages required by the barium salt of a dibromacrylic acid.

I. 1.0621 gram of the salt gave 0.4745 gram CO_2 and 0.0780 gram H_2O .

II. 1.0363 gram of the salt gave 0.4609 gram CO_2 and 0.0743 gram H_2O .

III. 0.6187 gram gave, on ignition with H_2SO_4 , 0.2415 gram BaSO_4 .

IV. 0.6180 gram gave 0.2434 gram BaSO_4 .

V. 0.5785 gram gave 0.2269 gram BaSO_4 .

VI. 0.3522 gram gave 0.1381 gram BaSO_4 .

Calculated for $\text{Ba}(\text{C}_3\text{HBr}_2\text{O}_2)_2$.

Found.

		I.	II.	III.	IV.	V.	VI.
C	12.10	12.19	12.14	...	...	...	...
H	0.34	0.82	0.80	...	...	...	...
Ba	23.03	...	...	22.95	23.15	23.05	23.05

Argentio Dibromacrylate, $\text{AgC}_3\text{HBr}_2\text{O}_3$. From the barium salt, or, better, from a solution of the free acid, the silver salt was made by the addition of argentic nitrate. It is precipitated in the form of fine, felted needles, even from a dilute solution of the acid; it may be recrystallized from hot water without any essential decomposition, and forms then long, flattened needles. The salt was dried over sulphuric acid for analysis.

I. 0.9755 gram substance gave 0.3890 gram of CO_2 and 0.0432 gram of H_2O .

II. 0.3200 gram substance gave, by the method of Carius, 0.3545 gram AgBr .

III. 0.7148 gram substance, precipitated with HBr , gave 0.4005 gram AgBr .

IV. 0.3668 gram gave, with HBr , 0.2056 gram AgBr .

Calculated for $\text{AgC}_3\text{HBr}_2\text{O}_3$.

		Found.			
		I.	II.	III.	IV.
C	10.69	10.87	...	...	...
H	0.30	0.49	...	...	...
Br	47.47	...	47.14	...	...
Ag	32.05	...	...	32.18	32.20

Plumbic Dibromacrylate, $\text{Pb}(\text{C}_3\text{HBr}_2\text{O}_3)_2$. The lead salt is precipitated in pearly rhombic scales by the addition of plumbic acetate to a solution of the free acid. It is readily soluble in hot water, sparingly in cold. When dried over sulphuric acid *in vacuo*, it gave:—

I. 0.3232 gram substance gave 0.1289 gram CO_2 and 0.0230 gram H_2O .

II. 0.4060 gram gave 0.1858 gram PbSO_4 .

III. 0.4908 gram gave 0.2230 gram PbSO_4 .

Calculated for $\text{Pb}(\text{C}_3\text{HBr}_2\text{O}_3)_2$.

		Found.		
		I.	II.	III.
C	10.82	10.86	...	...
H	0.30	0.79	...	...
Pb	31.13	...	31.27	31.05

Calcic Dibromacrylate, $\text{Ca}(\text{C}_3\text{HBr}_2\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$. On neutralizing a solution of the acid with calcic carbonate, and concentrating the solution on the water bath, the calcium salt was obtained in clusters of radiating needles, tolerably soluble even in cold water. The

salt gradually effloresced over sulphuric acid, and lost its crystal water completely at 80–85°.

0.7342 gram of the air-dried salt lost, at 80–85°, 0.0695 gram of H₂O.

Calculated for $\text{Ca}(\text{C}_3\text{HBr}_2\text{O}_2)_{1.5}\cdot 3\text{H}_2\text{O}$.		Found.
H ₂ O	9.78	9.47

0.4951 gram of the salt, dried at 80–85°, gave, on ignition with H₂SO₄, 0.1354 gram CaSO₄.

Calculated for $\text{Ca}(\text{C}_3\text{HBr}_2\text{O}_2)$.		Found.
Ca	8.03	8.04

Potassic Dibromacrylate, $\text{KC}_3\text{HBr}_2\text{O}_2$. The acid neutralized with potassic carbonate and evaporated gave, on cooling, crystals of the potassium salt. From neutral solutions it crystallizes in transparent, six-sided, clustered plates. If but a small amount of free acid is present, it crystallizes in fine, felted needles. Both forms are anhydrous, and do not lose in weight at 80°.

0.5506 gram gave, on ignition with H₂SO₄, 0.1792 gram K₂SO₄.

Calculated for $\text{KC}_3\text{HBr}_2\text{O}_2$.		Found.
K	14.58	14.61

An acid salt much less soluble in water may be made by adding acid to a solution of the potassium salt. It crystallizes in long needles, which are anhydrous. The salt is not particularly stable, and the excess of acid may be washed out with ether. The salt was dried by exposure to the air, after several recrystallizations from hot water.

I. 0.6116 gram substance gave, on ignition with H₂SO₄, 0.1151 gram K₂SO₄.

II. 0.5395 gram of substance gave 0.0959 gram K₂SO₄.

Calculated for $\text{KC}_3\text{HBr}_2\text{O}_2\cdot\text{C}_3\text{H}_2\text{Br}_2\text{O}_2$.		Found.	
K	7.85	I.	II.
		8.45	7.98

Dibromacrylic Acid. From the pure barium salt we set free the acid by the addition of hydrochloric acid, and extracted it from the solution with ether. The ether left, upon evaporation, a white, crystalline acid, which was very soluble in alcohol, ether, or chloroform, and but sparingly soluble in benzol, carbonic disulphide, or ligroin. Under water, it melted at about 20°, dissolved in every

proportion on heating, and was but slowly volatilized with steam. The acid, when melted under water, could be made to crystallize either by cooling with ice or by the addition of a mineral acid. After recrystallization from benzol, it melted at $83-84^{\circ}$, and this melting point we were unable to raise by further recrystallization from this or other solvents.

Although our analyses left no doubt of the formula of the substance, they showed that it was still impure.

I. 1.3074 gram substance gave 0.7692 gram CO_2 and 0.1121 gram H_2O .

II. 0.9833 gram substance gave 0.5797 gram CO_2 and 0.0877 gram H_2O .

III. 0.2042 gram gave 0.3366 gram AgBr.

IV. 0.2447 gram gave 0.4044 gram AgBr.

V. 0.2083 gram gave 0.3453 gram AgBr.

VI. 0.2005 gram gave 0.3309 gram AgBr.

VII. 0.2132 gram gave 0.3517 gram AgBr.

Calculated for $\text{C}_3\text{H}_3\text{Br}_2\text{O}_2$.

	I.		II.	III.	Found.		IV.	V.	VI.	VII.
C	15.65	16.04	16.08	...	...	...	...	...	...	...
H	0.87	0.95	0.99	...	...	...	...	...	...	...
Br	69.56	...	...	70.15	70.33	70.53	70.23	70.20		

Our results had sufficiently established the fact that a dibromacrylic acid was formed from mucobromic acid by the action of baric hydrate in the cold, but a more extended investigation of it was evidently needed to determine the nature of the impurity which was so difficult of removal. Since Wallach and Reincke¹ had shortly before announced that they were engaged in making from bromalid a dibromacrylic acid, which we thought probable, although upon very insufficient grounds, would prove to be identical with ours, we felt compelled for the moment to suspend our investigations. The other portions of the research afterward claimed so much attention that no study of the acid has yet been made sufficiently extended to establish the conditions essential to its preparation in a pure state. It has been found, however, that an acid melting at $84-85^{\circ}$ contains but a slight excess of bromine (I.), and that the pure acid (II.) melts at $85-86^{\circ}$.

I. 0.2204 gram substance gave 0.3621 gram AgBr.

¹ Berichte der deutsch. chem. Gesellsch. 10, 2128.

II. 0.2650 gram substance gave 0.4336 gram AgBr.

Calculated for $C_5H_3Br_2O_2$.

Br	Found.	
	I.	II.
69.56	69.90	69.65

For purposes of comparison, certain determinations of the solubility of the acid and its barium salt may find a place here, although they were not made with absolutely pure material, and are therefore subject to revision. In determining the solubility of the acid, the saturated solution, made according to the method of V. Meyer, was neutralized with baric carbonate, and the dissolved barium determined by precipitation with sulphuric acid.

I. 14.7798 grams of a solution, saturated at 20° , gave 0.4488 gram $BaSO_4$.

II. 8.6788 grams of a solution, saturated at 20° , gave 0.2630 gram $BaSO_4$.

According to these determinations, an aqueous solution of the acid, saturated at 20° , contains the percentages:

I.	II.
5.98	5.98

8.4992 grams of a solution of the barium salt, saturated at 20° , gave, on evaporation with H_2SO_4 and ignition, 0.1912 gram $BaSO_4$.

The aqueous solution of baric dibromacrylate, saturated at 20° , therefore contains 5.74 per cent. of the dry salt.

In studying the behavior of this dibromacrylic acid towards reagents, we have been able to use only the product melting at $83-84^\circ$, which may easily be obtained in any quantity desired. When boiled with an excess of baric hydrate, the acid is completely decomposed, baric carbonate is precipitated, bromacetylen set free, and at the same time baric malonate is formed in abundance. For complete identification, the baric malonate was converted into the lead salt, and the latter analyzed.

0.5179 gram of the salt, dried at 110° , gave, on ignition with H_2SO_4 , 0.5062 gram $PbSO_4$.

Calculated for $PbC_3H_3O_4$.

66.99

Found.

66.79

The amount of baric malonate formed in this decomposition with an excess of baric hydrate was found to be forty-nine per cent. of the theoretical yield as the mean of two determinations.

The behavior of the acid towards hydrobromic acid was studied by Mr. C. F. Mabery. It is not altered by ordinary concentrated hydrobromic acid (b. pt. 126°), nor is it affected in the cold by an acid saturated at 0° ; but it forms an addition-product when heated with it for several hours at 100° . The reaction is by no means neat, and a large portion of the substance is charred. The tribromopropionic acid which is thus formed differs essentially in its melting-point ($116-117^{\circ}$) and other physical properties from the acid melting at 93° mentioned by Linneman and Penl,¹ and recently more fully described by Michael and Norton;² and also from the acid melting at 53° , which was obtained by Fittig and Petri,³ by the action of hydrobromic acid upon their dibromacrylic acid. It is sparingly soluble in cold water, readily in hot, and may be crystallized without difficulty from hot water. It is readily soluble in alcohol or ether, somewhat less soluble in chloroform. From water it crystallizes in pearly scales, which melt at $116-117^{\circ}$. Argentic nitrate precipitates from an aqueous solution of the acid, the silver salt in clustered rhombic plates.

0.1892 gram of the acid gave 0.3453 gram AgBr.

	Calculated for $C_3H_3Br_3O_2$.	Found.
Br	77.16	77.64

If one molecule of bromine is added to dibromacrylic acid dissolved in chloroform, the color of the bromine gradually disappears, and after the lapse of some time tetrabromopropionic acid separates in large, well-formed crystals, which melt at 125° . This acid is at present under investigation in this laboratory.

One well-marked product of the decomposition of mucobromic acid by cold baric hydrate had been shown to be baric dibromacrylate; it only remained to study the more soluble products of the reaction. In continuing the investigation with Mr. O. R. Jackson, the filtrate from the crystals of baric dibromacrylate was treated with carbonic dioxide to remove the excess of baric hydrate, filtered from the baric carbonate, and the filtrate evaporated at a gentle heat ($40-50^{\circ}$). In the course of this evaporation, a certain amount of baric dibromacrylate crystallized out, which was removed from time to time. When the liquid had been reduced to about one-third its original volume, it was precipitated by the addition of

¹ Berichte der deutsch. chem. Gesellsch. **8**, 1098.

² Amer. Chem. Journ. **2**, 18.

³ Ann. Chem. u. Pharm. **195**, 73.

two volumes of alcohol. The bulky crystalline precipitate thus thrown down proved upon qualitative examination to consist chiefly of baric formiate. When purified by repeated precipitation from aqueous solution by alcohol and recrystallization from water, it showed the characteristic form of baric formiate.

0.3964 gram substance gave, on ignition with H_2SO_4 , 0.4054 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{CHO}_2)_2$.	Found.
Ba	60.36	60.13

The lead salt made from the barium salt crystallized in the characteristic form of plumbic formiate, and gave on analysis the required percentage of lead.

0.4149 gram of the salt gave, on ignition with H_2SO_4 , 0.4221 gram PbSO_4 .

	Calculated for $\text{Pb}(\text{CHO}_2)_2$.	Found.
Pb	69.69	69.50

In the alcoholic filtrate from the baric formiate, we were able to find, beside baric bromide, only a crystallizable barium salt, well marked by its qualitative reactions, but so unstable that we were not able to effect its purification. The behavior of this salt, and the analyses which we made of it in an impure state, led us to the conclusion that it was the barium salt of brompropionic acid, formed by subtraction of hydrobromic acid from the dibromacrylic; and this view was subsequently proved to be correct by a study of the addition products which the corresponding acid formed with the halogens and the haloid acids.

Since all our attempts to isolate a pure salt from a solution containing baric bromide had proved unsuccessful, we attempted to take advantage of a remarkably stable molecular compound which the corresponding acid forms with dibromacrylic acid. This compound may readily be made by acidifying the baric hydrate solution of mucobromic acid, without removing the separated baric dibromacrylate, and extracting the solution with ether. The same compound, although in smaller quantity, may also be obtained, after that portion of the barium salt which separates spontaneously is removed. From dibromacrylic acid it may be made by the action of baric hydrate in the cold. For its preparation we usually have employed a solution of potassic, instead of baric, hydrate. The proportions which we have found most advantageous are 70

grams of potassic hydrate and 400 cc. of water to 100 grams of mucobromic acid. Care must be taken in adding the mucobromic acid, and also in the subsequent acidification with hydrochloric acid, that no sensible elevation of temperature takes place. When the solution is partially acidified, the acid potassium salt of dibromacrylic acid usually separates in abundance, but dissolves upon further addition of acid. The solution is then thoroughly extracted with ether; and this leaves on distillation a liquid residue, which, on cooling, gradually solidifies in large, well-formed, monoclinic (?) prisms. These are readily soluble in water, alcohol, ether, or chloroform, and may be purified by crystallization from hot benzol, or more conveniently by melting with a little water. Thus purified, the substance melts at $104-105^{\circ}$; and this melting point is not altered by repeated recrystallizations from various solvents.

I. 0.9023 gram substance gave 0.6440 gram CO_2 and 0.0850 gram H_2O .

II. 0.4403 gram substance gave 0.3157 gram CO_2 and 0.0433 gram H_2O .

III. 0.2263 gram substance gave 0.3386 gram AgBr .

IV. 0.2241 gram substance gave 0.3321 gram AgBr .

V. 0.2092 gram substance gave 0.3139 gram AgBr .

Calculated for $\text{C}_8\text{H}_3\text{Br}_3\text{O}_4$.			Found.			
		I.	II.	III.	IV.	V.
C	19.00	19.43	19.54	...	...	...
H	0.79	1.05	1.09	...	...	...
Br	63.33	...	...	63.66	63.03	63.84

Although the percentages we have found show a considerable variation from those calculated for equal molecules of dibromacrylic and brompropionic acids, they agree better with this than with any other formula equally simple; and, moreover, the qualitative behavior of the substance is such as to render this formula tolerably certain. Its aqueous solution gives, on the addition of plumbic acetate, an immediate crystalline precipitate of plumbic dibromacrylate.

0.3560 gram gave, on ignition with H_2SO_4 , 0.1628 gram PbSO_4 .

Calculated for $\text{Pb}(\text{C}_3\text{HBr}_2\text{O}_2)_2$.		Found.
Pb	31.13	31.25

So also if it is neutralized with baric carbonate, the solution gives, on spontaneous evaporation, crystals of baric dibromacrylate, while in solution remains a much more soluble salt, with all the characters of baric brompropionate. That this substance contains the brompropionic acid is shown by the evolution of carbonic dioxide and bromacetylen when its aqueous evolution is boiled.

Starting with this molecular compound melting at $104-105^{\circ}$, we made various attempts to isolate the brompropionic acid and its salts in a pure state. The barium salts of dibromacrylic and brompropionic acids showed such marked differences in their solubility in water or in alcohol that we hoped through them to effect a complete separation of the two acids. We found, however, that it was difficult to obtain in this way a colorless salt of brompropionic acid which appeared even tolerably pure. We therefore attempted to separate the two acids by converting them into their ethyl-ethers and submitting these to fractional distillation. We dissolved the molecular compound (m. pt. 104°) in absolute alcohol, added concentrated sulphuric acid, and warmed. The ethers soon separated in part, and were precipitated with water, washed with dilute sodic carbonate, and dried over fused calcic chloride. These mixed ethers had an extremely sharp, pungent odor, and their vapor attacked the eyes violently. On attempting to separate the two by distillation, we found that a large portion of the liquid was carbonized in each distillation, and that but one volatile product could be isolated. This was a mobile liquid, of an agreeable aromatic odor, which boiled between 209 and 215° , without any very noticeable decomposition. The portion of this which boiled between $212-214^{\circ}$ was analyzed, and found to be essentially the ethyl-ether of dibromacrylic acid, although still impure. Since our chief object was to isolate the ether of the brompropionic acid, and this had evidently been for the most part destroyed, the substance was not farther examined.

0.5235 gram of substance gave, on combustion, 0.4675 gram CO_2 and 0.1250 gram H_2O .

	Calculated for $\text{C}_3\text{HBr}_2\text{O}_2 \cdot \text{C}_2\text{H}_5$.	Found.
C	23.23	24.36
H	2.33	2.65

Finally, we attempted to separate the two acids by fractional saturation. Although the products thus obtained gave us analy-

tical results that were far from satisfactory, we found that the separation could be effected with tolerable precision, the bromopropiolic acid being the stronger acid, and that this was the most convenient way of preparing material sufficiently pure for further work, in any considerable quantity. Pure substance melting at $104-105^{\circ}$ was dissolved in water, and a little less than the calculated amount of baric carbonate was added. The clear solution was then freed as completely as possible from dibromacrylic acid by repeated extraction with ether, and the baric bromopropiolate obtained by spontaneous evaporation.

Our analytical results show that the material analyzed was not pure, and yet they leave no doubt as to its nature.

I. 0.6974 gram of substance, dried over H_2SO_4 , gave 0.3968 gram CO_2 and 0.0347 gram H_2O .

II. 0.3060 gram of substance, dried over H_2SO_4 , gave 0.1657 gram $BaSO_4$.

III. 0.1829 gram of substance, dried over H_2SO_4 , gave 0.0973 gram $BaSO_4$.

IV. 0.4325 gram of substance, dried over H_2SO_4 , gave 0.2305 gram $BaSO_4$.

Calculated for $Ba(C_3BrO_2)_2$.		Found.			
		I.	II.	III.	IV.
C	16.63	15.52	...	...	...
H	...	0.55	...	...	...
Ba	31.63	...	31.84	31.27	31.32

We have been unable to make any satisfactory determinations of the water of crystallization, since the salt cannot be heated, and even on standing over sulphuric acid in the cold it is slowly decomposed. The salt when crystallized from water probably contains four molecules of water.

I. 2.1104 gram of the air-dried salt lost over sulphuric acid 0.2803 gram.

II. 0.9828 gram of air-dried substance lost over H_2SO_4 0.1316 gram.

Calculated for $Ba(C_3BrO_2)_2 \cdot 4H_2O$.		Found.	
		I.	II.
H_2O	14.26	13.28	13.39

In one instance the salt precipitated from alcoholic solution by the addition of ether was found to contain but a single molecule of water.

1.0639 gram of air-dried salt lost over H_2SO_4 *in vacuo* 0.0458 gram.

Calculated for $\text{Ba}(\text{C}_3\text{BrO}_2)_2 \cdot \text{H}_2\text{O}$.		Found.
H_2O	3.99	4.30

The salt usually crystallized, on the slow evaporation of its aqueous solution, in small, oblique prisms; but it sometimes separated, on long standing, in more compact, clustered, rhombic plates. When dry, it is decomposed quite rapidly at 50° , and deflagrates at about 125° . In aqueous solution it is recomposed on boiling, with the precipitation of baric carbonate and the evolution of carbonic dioxide and bromacetylen. From solutions containing an excess of the acid, a somewhat more stable salt separates in fine, felted needles, less soluble in water than the neutral salt. This would seem to be an acid salt, corresponding to the acid potassium salt of dibromacrylic acid; but we could obtain no satisfactory analytical results.

When argentic nitrate is added to a solution of the barium salt, or of the free acid, a white, amorphous silver salt is precipitated, and at the same time if the solution is concentrated the evolution of carbonic dioxide is noticed. The precipitate turns yellow on washing, and is evidently still further decomposed on drying. When gently warmed with water, it is slowly decomposed; but, when suddenly heated nearly to 100° , it explodes violently, with the separation of large quantities of carbon. In a dry state it explodes when heated to about 75° . In dilute nitric acid it dissolves at first; but the solution soon grows turbid, smells strongly of bromacetylen, and argentic bromide is precipitated. One could hardly expect trustworthy results from the analysis of so unstable a substance. One silver determination, however, showed that it must be considered a derivative of bromacetylen, rather than of brompropionic acid.

0.2313 gram of substance, dried over H_2SO_4 *in vacuo*, gave 0.1975 gram AgBr.

Calculated for AgC_3BrO_2 ; for AgC_3Br .		Found.
Ag	42.19	49.94

Although the barium salt had given unsatisfactory results on analysis, we made from it the acid, and hoped then to be able to effect its purification. We therefore precipitated the barium from a cold, aqueous solution, with a slight excess of sulphuric acid, and

extracted the acid from the filtered solution with ether. We obtained in this way long, slender prisms, extremely soluble in water, alcohol, or ether, readily in chloroform or benzol, more sparingly in carbonic disulphide, and but slightly soluble in ligroin. The crystals obtained from aqueous solution by spontaneous evaporation appeared to contain water of crystallization. When pressed with paper they melted at $60-65^{\circ}$; but over sulphuric acid they soon became opaque, and the melting point had risen to 80° or over.

We attempted the purification of the acid by repeated recrystallization from ligroin to which a little ether had been added. The long, silky needles thus obtained melted at 86° , but gave on analysis no satisfactory results (I. and II.). Although the acid was blackened and apparently completely decomposed at a temperature but little over 100° , we found that it could be sublimed readily between watch-glasses at steam heat. The melting point was, however, lowered rather than raised, by successive sublimations, and analyses (III. and IV.) of the sublimed product gave too high a percentage of bromine.

I. 0.3010 gram substance gave 0.4025 gram AgBr.

II. 0.1198 gram substance gave 0.1582 gram AgBr.

III. 0.2010 gram substance gave 0.2580 gram AgBr.

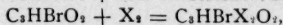
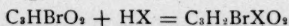
IV. 0.1820 gram substance gave 0.2339 gram AgBr.

Calculated for C_3HBrO_3 .

Found.

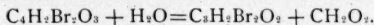
		I.	II.	III.	IV.
Br	53.69	56.90	56.21	54.63	54.69

The acid is decomposed, with the formation of carbonic dioxide and bromacetylen, on boiling its aqueous solution. When heated with an excess of baric hydrate, baric carbonate is precipitated, bromacetylen is evolved, and at the same time baric malonate is formed in abundance. It unites with dibromacrylic acid immediately to form the characteristic addition-product. An ethereal solution containing a mixture of the two acids, approximately in molecular proportions, gave on evaporation a substance which, without purification, melted at 103° . With the halogens and haloid acids, it forms addition products with the greatest readiness. The substituted acrylic acids which are thus formed, according to the equations,—

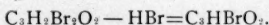


are easily purified, and their formation can leave no doubt of the nature of the brompropionic acid. Several of these acids will be described later in this paper.

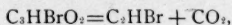
The decomposition of mucobromic acid by baric hydrate, under the conditions described, may be expressed by the following equations. The first action would seem to be the assimilation of a molecule of water and the formation of dibromacrylic and formic acids.



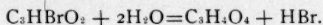
This action is immediately followed, even in the cold, by the subtraction of hydrobromic acid,—



The brompropionic acid is then either decomposed by heat,—



or is converted into malonic acid,—



Since a large percentage of dibromacrylic acid was converted into brompropionic acid in this reaction, and it had previously been proved that a portion of the mucobromic acid entirely escaped decomposition when the proportion of baric hydrate was materially lessened, I recently attempted to increase the yield by reversing the mode of procedure. I therefore added baric hydrate, gradually, to mucobromic acid suspended in a little water; taking care, after the acid was neutralized, to make the solution but slightly alkaline, and to wait until it was again neutral before further addition. I found, however, that an entirely different reaction had taken place under these conditions, and that among the products of this reaction little or no dibromacrylic acid could be found. This decomposition is at present under investigation in this laboratory, and all discussion of the results we have already obtained must therefore be reserved for a subsequent paper.

(*To be continued.*)

XI.—ON THE DIIODBROMACRYLIC AND CHLOR-BROMACRYLIC ACIDS.¹

BY C. F. MABERY AND RACHAEL LLOYD.

The readiness with which brompropionic acid unites with the halogens and the haloid acids to form members of the acrylic acid series has been described by Prof. H. B. Hill,² and certain of these addition products have been studied in detail by him and one of us.³

The products which result by the action of iodine and of hydrochloric acid on brompropionic acid will be described in this paper.

DIIIODBROMACRYLIC ACID, $C_3I_2BrO_2H$.

Diiodbromacrylic acid is formed when brompropionic acid is allowed to stand for some time with a solution of iodine in ether. As this method of preparation was found to be somewhat tedious from the length of time required to complete the reaction, we tried the effect of raising the temperature. Brompropionic acid, with a slight excess over the calculated weight of iodine and five parts by weight of ether, was heated for two hours under a return condenser on the water bath. The residue left after the evaporation of the ether was extracted with successive portions of warm water, and the solution concentrated by evaporation. Diiodbromacrylic acid was deposited from this solution, on cooling, in glistening plates, which were purified by recrystallization from hot water.

The yield of pure product by this method has been about sixty per cent. of the amount theoretically required. The mother liquors of the first crystallization gave by evaporation an oily product, which solidified on standing, but which could be purified only with considerable difficulty. This substance crystallizes in flat, white, six-sided plates, very sparingly soluble in cold water, readily in hot, and very soluble in ether, alcohol, carbonic disulphide, and ligroin. It melts at 160° , and sublimes slowly at higher temperatures, apparently unchanged. A yellow coating is formed on the surface when it is exposed to the action of light, yet the decomposition by nitric acid in the estimation of the halogens is not complete below 300° .

¹ Communicated by the Authors. This research was conducted in connection with the Summer Course of Instruction in Chemistry at Harvard College. C. F. M.

² *Berichte der deutsch. chem. Gesellsch.* **12**, 660.

³ *Amer. Acad. Proc.* **16**, 211.

The following results were obtained by analysis:

0.5188 gram substance gave 0.1682 gram CO_2 and 0.0180 gram H_2O .

0.2004 gram substance gave by Carius' method 0.3276 gram $\text{AgI} + \text{AgBr}$.

	Calculated for $\text{C}_3\text{I}_2\text{BrO}_2\text{H}$.	Found.
C	8.93	8.84
H	.25	.39
$\text{I}_2 + \text{Br}$	82.87	82.96

The solubility in cold water was determined by the method of V. Meyer. The filtered solution was neutralized with baric carbonate, evaporated to dryness, and the barium estimated by ignition with sulphuric acid.

I. 11.7286 grams solution gave 0.0707 gram BaSO_4 .

II. 13.3239 grams solution gave 0.0793 gram BaSO_4 .

The solution, saturated at 20° , contains, therefore, the percentages:

I.	II.
2.08	2.05

Hence diiodbromacrylic acid requires for solution 48.37 parts water at 20° .

SALTS OF DIIODBROMACRYLIC ACID.

Baric Diiodbromacrylate, $\text{Ba}(\text{C}_3\text{I}_2\text{BrO}_2)_2 \cdot 4\text{H}_2\text{O}$. A solution of the acid was heated with an excess of baric carbonate, filtered, and concentrated by evaporation. The salt crystallized, on cooling, in flat prisms arranged in stellate groups. It is very soluble in hot, less soluble in cold, water.

I. 0.8805 gram air-dried salt gave 0.0638 gram H_2O at 80° .

II. 0.8981 gram air-dried salt gave 0.0629 gram H_2O at 80° .

III. 0.8049 gram anhydrous salt gave 0.2002 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_3\text{I}_2\text{BrO}_2)_2 \cdot 4\text{H}_2\text{O}$.	I.	Found.	II.
H_2O	7.11	7.24		7.00
	Calculated for $\text{Ba}(\text{C}_3\text{I}_2\text{BrO}_2)_2$.		Found.	
Ba	14.55		14.62	
IO				

To determine the solubility in cold water, a hot solution was kept at 20° for four hours, with occasional stirring. The filtered solution was evaporated to dryness, and the barium estimated by ignition with sulphuric acid.

I. 3.2417 grams solution gave 0.1218 gram BaSO_4 .

II. 7.0500 grams solution gave 0.2665 gram BaSO_4 .

This solution contains, therefore, the following percentages:

I.	II.
15.17	15.26

Taking the mean of these results, this salt requires for solution 6.571 parts water at 20°.

Calcic Diiodbromacrylate, $\text{Ca}(\text{C}_3\text{I}_2\text{BrO}_2)_2$. This salt was prepared by neutralizing a solution of the acid with calcic carbonate, and evaporating the filtered solution. The salt crystallizes in branching needles, which are very soluble in water.

0.5995 gram of the air-dried salt lost 0.0031 gram at 80°.

This was probably due to the presence of a trace of hygroscopic moisture.

0.5964 gram of the salt, dried at 80°, gave 0.0945 gram CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_3\text{I}_2\text{BrO}_2)_2$.	Found.
Ca	4.74	4.66

Argentio Diiodbromacrylate, $\text{AgC}_3\text{I}_2\text{BrO}_2$. Argentio nitrate, added to a solution of the acid, caused a voluminous precipitate of the silver salt, which was washed and dried over sulphuric acid for analysis. It forms oblique prisms, very slightly soluble in cold water, but readily soluble in dilute nitric acid.

0.9585 gram salt gave 0.2677 gram AgCl .

	Calculated for $\text{AgC}_3\text{I}_2\text{BrO}_2$.	Found.
Ag	21.17	21.02

Potassic Diiodbromacrylate, $\text{KC}_3\text{I}_2\text{BrO}_2 \cdot 2\text{H}_2\text{O}$. A solution of the acid was neutralized with potassic carbonate, and evaporated on the water bath. On cooling, the salt separated in the form of oblique prisms, which are quite soluble in water.

1.8818 gram of the air-dried salt gave 0.1381 gram H_2O at 80°.

1.7460 gram anhydrous salt gave 0.3347 gram K_2SO_4 .

Calculated for $KC_3I_2BrO_2 \cdot 2H_2O$.		Found.
H ₃ G	7.55	7.33
Calculated for $KC_3I_2BrO_2$.		Found.
K	8.87	8.50

CHLORBROMACRYLIC ACID, $C_3ClBrO_2H_2$.

Chlorbromacrylic acid may be made by the action of ordinary fuming hydrochloric acid on brompropionic acid. This reaction, however, takes place slowly in the cold; and, although the application of heat causes a more rapid formation of the chlorbromacrylic acid, it produces a secondary decomposition which renders the purification of the product somewhat difficult. We therefore tried the action of hydrochloric acid saturated at 0° . The acid solution soon became filled with crystals of the addition product; and after standing twenty-four hours the reaction was complete. The excess of hydrochloric acid was removed by decantation, and by pressure between folds of filter paper, and the chlorbromacrylic acid was purified by crystallization from hot water. It separates as an oily liquid from a hot aqueous solution; but when nearly cold it crystallizes, forming elongated, flat prisms or needles.

This acid melts at 70° , and sublimes quite freely at a somewhat higher temperature. It is much more soluble in hot than in cold water, and readily soluble in ether, alcohol, benzol, and carbonic disulphide. Its composition was determined by the following analyses:—

0.4462 gram substance gave 0.3126 gram CO_2 and 0.0337 gram H_2O .

0.1792 gram substance gave, by the method of Carius, 0.3186 gram $AgCl + AgBr$.

Calculated for $C_3ClBrO_2H_2$.		Found.
C	19.40	19.11
H	1.08	.34
Cl+Br	62.26	61.94

The solubility of this acid in cold water was determined by the same method as the diiodbromacrylic acid.

I. 11.6861 grams solution gave 0.4178 gram BaSO_4 .

II. 14.4534 grams solution gave 0.5264 gram BaSO_4 .

The solution, saturated at 20° , contains the percentages:

I.	II.
5.69	5.80

The mean of these results gives 17.41 parts as the quantity of water required for solution at 20° .

SALTS OF CHLORBROMACRYLIC ACID.

The salts of this acid were made by the same methods as the corresponding salts of diiodbromacrylic acid.

Baric Chlorbromacrylate, $\text{Ba}(\text{C}_3\text{ClBrO}_2\text{H})_2 \cdot 2\text{H}_2\text{O}$. This salt crystallizes in flattened prisms, which belong apparently to the monoclinic system. Its composition was established by the following analyses:

- I. 0.3730 gram air-dried salt gave 0.0263 gram H_2O at 80° .
- II. 0.6283 gram air-dried salt gave 0.0437 gram H_2O at 80° .
- III. 0.3467 gram anhydrous salt gave 0.1606 gram BaSO_4 .
- IV. 0.4468 gram anhydrous salt gave 0.2053 gram BaSO_4 .

Calculated for $\text{Ba}(\text{C}_3\text{ClBrO}_2\text{H})_2 \cdot 2\text{H}_2\text{O}$.		Found.	
		I.	II.
H_2O	6.64	7.05	6.96
Calculated for $\text{Ba}(\text{C}_3\text{ClBrO}_2\text{H})_2$.		Found.	
		III.	IV.
Ba	27.07	27.23	27.02

The solubility in cold water was determined by the method of V. Meyer.

I. 2.8936 grams solution gave 0.1914 gram BaSO_4 .

II. 5.1385 grams solution gave 0.3378 gram BaSO_4 .

From these results the following percentages were calculated:

I.	II.
14.06	14.28

This salt, therefore, requires for solution 6.985 parts of water at 20° .

Calcic Chlorbromacrylate, $\text{Ca}(\text{C}_3\text{ClBrO}_2\text{H})_2 \cdot 4\text{H}_2\text{O}$. This salt forms branching needles, which are very soluble in hot, less soluble in cold, water.

- I. 0.4981 gram air-dried salt gave 0.0762 gram H_2O at 80° .
 II. 0.6211 gram air-dried salt gave 0.0956 gram H_2O at 80° .
 III. 0.4219 gram anhydrous salt gave 0.1424 gram $CaSO_4$.
 IV. 0.5096 gram anhydrous salt gave 0.1713 gram $CaSO_4$.

Calculated for $Ca(C_3ClBrO_2H)_2 \cdot 4H_2O$.		I.	Found.	II.
H_2O	14.97	15.30		15.39
Calculated for $Ca(C_3ClBrO_2H)_2$.		III.	Found.	IV.
Ca	9.78	9.93		9.87

Argentie Chlorbromacrylate, $Ag(C_3ClBrO_2H)_2$. This salt was precipitated by the addition of argentic nitrate and ammoniac hydrate to a solution of the acid. It forms microscopic needles, which are almost insoluble in cold water.

- I. 0.2760 gram salt gave 0.1337 gram $AgCl$.
 II. 0.3445 gram salt gave 0.1668 gram $AgCl$.

Calculated for $Ag(C_3ClBrO_2H)_2$.		I.	Found.	II.
Ag	36.93	36.47		36.88

Potassic Chlorbromacrylate, KC_3ClBrO_2H . This salt forms clusters of irregular, pointed, anhydrous prisms, which are less soluble in cold than in hot water.

0.5346 gram salt, dried at 80° , gave 0.2132 gram K_2SO_4 .

Calculated for KC_3ClBrO_2H .		Found.
K	17.49	17.91

The addition of bromine to chlorbromacrylic acid takes place very readily at the ordinary temperature, with the formation of chlortribrompropionic acid. A solution of the acid in chloroform was allowed to stand several days, with somewhat more than the calculated weight of bromine. Chlortribrompropionic acid separated from this solution in large prismatic crystals, which after crystallization from carbonic disulphide melted at about 98° . This acid will be submitted to a more extended study.

ON MICROLITE FROM AMELIA CO., VIRGINIA.

BY F. P. DUNNINGTON.

The mineral which is the subject of this examination was collected at the mica mines, two miles north of Amelia C.H., by Prof. W. M. Fontaine of this University, who gives the following notes of its occurrence and associations:

"This mineral occurs with others imbedded in a vein of 'Gigantic Granite,' (so called because of the essential minerals of the granite being crystallized in large masses) which is enclosed in gneiss and mica schist, with the general characters of the Montalban series. Schorl is very abundant in the adjoining wall-rock.

"The associated minerals are as follows:

"Beryl, abundant, sometimes in large crystals eight to ten inches in diameter; fluorite and columbite, not uncommon; amethystine quartz, occasional; apatite, rare. In addition to which are the large crystal masses composing the vein, quartz, orthoclase¹ and mica (of which last the sheets are frequently three feet across, and for which the vein is worked)."

Prof. Fontaine presumed the mineral in question would prove of interest, and handed it over to me for further examination, the result of which is as follows:

It is found in single crystals varying in dimensions from one-tenth to three-quarters of an inch, and in larger crystalline masses of which one was obtained weighing *eight pounds*. It occurs crystallized in octahedra of the Isometric system, some of the edges of which measure two centimetres; the face 1 is principally developed, and with it are the truncations made by O, 3-3 and *i* (Dana).

It has the following properties: Hardness, a little less than 6; specific gravity, 5.656; lustre, glistening resinous; color, wax yellow to brown; streak, pale ochreous yellow; subtranslucent; fracture conchoidal and very brittle.

Heated in a closed tube it decrepitates and gives off a little water. When ignited it glows momentarily as if taking fire. Before the blow-pipe it colors the flame a reddish yellow, is infusible, and on cooling is colored pale yellow and is without lustre. With the borax bead and also with that of salt of phosphorus, in both flames it gives a glass, yellowish when hot, colorless when cold. In both flames the saturated bead of salt of phosphorus is yellow when hot and greenish-yellow when cold. It is not attacked by strong

¹ Ratio of potash to soda=11 to 4.—F. P. D.

hydrochloric acid, but is decomposed slowly by concentrated sulphuric acid and also by fusion with caustic potash. It is readily decomposed by fusion with acid potassium sulphate. Fused with potassium nitrate and sodium carbonate, it does not give the manganese reaction. The moist metallic acids boiled with hydrochloric acid and tin afford a pale blue color.

The finely pulverized mineral was fused at a low red heat in a platinum crucible with eight parts of acid potassium sulphate. Four portions of about two grams each were thus fused, and all the constituents except the acids, alkalies and water, were then determined from the sum of these = 8.3370 grams of the mineral.

The metallic acids, insoluble in dilute hydrochloric acid, were well washed and then digested with yellow ammonium sulphide and washed, and then *separately* washed with dilute hydrochloric acid and finally washed with water. The oxides of tin and tungsten obtained from the ammonium sulphide solution were weighed together, then fused with sodium carbonate and a little potassium cyanide and washed. The tin dissolved out by hydrochloric acid, reprecipitated by hydrogen sulphide, washed, ignited and weighed, the tungsten being obtained by difference.

The insoluble metallic acids were treated with hydrofluoric acid and acid potassium fluoride, HKF_2 , and the double salt, $2\text{KF} \cdot \text{TaF}_5$, crystallized out according to Marignac's process; the crystals obtained were washed free of niobium and then dissolved and recrystallized. The washings and mother liquors were evaporated to a small bulk, and the crystals so obtained purified as before, and finally the filtrate again treated as before, there being obtained from one portion:

Ta_2O_5 , 4.844. Sp. gr. = 7.77, and after prolonged ignition = 7.96.

$^1 \text{Nb}_2\text{O}_5$, .558.

giving the ratio 8.68 to 1.

And from another portion:

$^2 \text{Ta}_2\text{O}_5$, 5.189

Nb_2O_5 , .577. Sp. gr. 4.20, and after prolonged ignition = 4.23,
giving the ratio 9 to 1.

The mean of these determinations gives the ratio by weight:

Ta_2O_5 to Nb_2O_5 = 8.84 to 1.

If these oxides when mixed do not change their volume on ignition, the mixed acids as separated should have had sp. gr. = less

¹ Containing some Ta_2O_5 .

² Containing some Nb_2O_5 .

than 7.6, whereas after prolonged ignition they had sp. gr.=7.86. I propose therefore to further examine this apparent combination of so closely related elements.

All the above specific gravities were taken between 11° and 14° C., and referred to water at this temperature.

The cerium metals proved to be present in too small amount to admit of accurate separation; they consist in about equal portions of cerium and didymium, and probably entirely of these, as lanthanum was not identified.

None of the lines attributed to erbium were found with the earths of the yttria group.

A portion dissolved in sulphuric acid under carbon dioxide decolorized a very little potassium permanganate corresponding in amount to and probably due to the cerium as cerous oxide (Ce_2O_3), therefore the uranium and iron are taken as U_2O_3 and Fe_2O_3 .

Fluorine was estimated by the volumetric method of Mr. S. L. Penfield,¹ and since, in order to decompose the mineral, the sulphuric acid was heated to 175° C. and for many hours, I took special precautions to condense the volatilized sulphuric acid and then deducted the minute amount of sulphuric acid found in the titrated liquid.

The water was given off below a red heat.

No trace of lead or of manganese was found.

The analysis gave the following results:

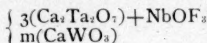
Ta_2O_5	.	.	.	.	.	68.43
Nb_2O_5	.	.	.	.	.	7.74
WO_3	.	.	.	.	.	.30
SnO_2	.	.	.	.	.	1.05
CaO	.	.	.	.	.	11.80
MgO	.	.	.	.	.	1.01
BeO	.	.	.	.	.	.34
U_2O_3	.	.	.	.	.	1.59
Y_2O_3	.	.	.	.	.	.23
Ce_2O_3	}	.	.	.	.	.17
Di_2O_3		.	.	.	.	.17
Al_2O_3	.	.	.	.	.	.13
Fe_2O_3	.	.	.	.	.	.29
Na_2O	.	.	.	.	.	2.86
K_2O	.	.	.	.	.	.29
F	.	.	.	.	.	2.85
H_2O	.	.	.	.	.	1.17
						100.25
Deduct O replaced by F	.	.	.	.	.	1.20
						99.05

¹ This Journal, 1, 27.

Considering the bases as replacing equivalent amounts of calcium and neglecting the water, we have the following atomic relations:

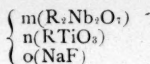
Ca	Ta	Nb	Sn & W	F	O
32.9	30.9	5.8	.83	15	118.6

If we exclude the Fe_2O_3 and Al_2O_3 as uncombined, as they most probably are, the following formula may be deduced:



It may be remarked that in *most* of the reported analyses of pyrochlore, the fluorine and alkaline metals nearly correspond in number of atoms, which is clearly not so in this case, while the relation between the niobium and fluorine points to the association of these elements under the familiar form of NbOF_3 .

To some of the analyses of pyrochlore, considered by Prof. C. Rammelsberg in his extended paper¹ on tantalates and niobates, he assigns the formula:



From the results of the above analysis and also from its crystalline habit, it therefore appears that this mineral is the one which has been described by Prof. C. U. Shepard as microlite, although it proves to have a composition different from that originally supposed by him, and corresponding to that suggested by Prof. Brush, viz: essentially a calcium tantalate.

The minute size of the crystals in which it was previously found fully warranted the name microlite, but in view of the present facts it appears rather inappropriate.²

UNIVERSITY OF VIRGINIA, Apr. 1881.

¹ Journal Chem. Soc. Ser. 2, 10, 203.

² A private communication from Prof. E. S. Dana informs me of a recent analysis by Norden-skiöld, of a mineral from Utö, in size of crystals a true microlite, who found in it: $\text{Ta}_2\text{O}_5(\text{Nb}_2\text{O}_5)$, 77.3; SnO_2 , 0.8; CaO , 11.7; MuO , FeO , 7.7; MgO , 1.8; total, 99.3.

F. P. D.

ON THE CONDUCT OF FINELY DIVIDED IRON
TOWARDS NITROGEN.

BY IRA REMSEN.

A recent writer¹ states that the method of Lassaigne for the detection of nitrogen in bodies containing carbon is not applicable to compounds in which sulphur is present. He claims that the sulphur gives rise to the formation of sulphocyanide, and that this is overlooked, as the solutions are strongly acid. A list of compounds is given in which nitrogen can not be detected. It includes taurine, sulpho-urea, sulphocyanide of potassium, and the "amides of the sulphonic acids." In such cases it is recommended to fuse the bodies with sodium and pure iron, instead of sodium alone, as is customary. The sulphur forms sulphide of iron, and the nitrogen forms the cyanide and can easily be detected.

As I have repeatedly used the ordinary method for the detection of nitrogen in compounds containing sulphur, and have in some cases relied upon the results reached, I undertook an examination of the subject thus opened, and I have been led to conclusions directly opposed to those of the writer referred to. At the same time certain interesting observations have been made on the conduct of pure iron, reduced by hydrogen, towards nitrogen.

As regards the statement that the method of Lassaigne is not applicable to compounds containing sulphur, I am prepared to give this an unqualified denial. I have examined every one of the substances mentioned by the writer, with the exception of cystine, and have in each case without the slightest difficulty obtained the precipitate of Prussian blue. I have also examined a large number of other substances, and have never experienced difficulty in getting the result looked for. Then, further, the fact that sulphocyanide of sodium or potassium itself breaks up under the influence of heat in the presence of an alkaline metal shows clearly that, even if this salt is formed as is claimed and as is probable, the detection of the nitrogen can not be interfered with by the presence of sulphur.

Having shown beyond a doubt that the conclusion I had drawn with reference to a certain compound, that it contained no nitrogen,

¹ *Berichte d. deutsch. chem. Gesell.* 12, 2316.

is correct, I nevertheless fused a small specimen of this compound with sodium and iron by hydrogen, and was astonished to find that, on extracting the fused mass with water, filtering and then adding successively ferric and ferrous salts and hydrochloric acid, the blue precipitate revealing the presence of nitrogen was distinctly formed. I repeated the experiments a number of times, but always with practically the same result. In every case the blue precipitate was formed, though in some cases it seemed to be formed in larger quantity than in others. The variations in quantity were, however, not striking.

I now took other non-nitrogenous organic substances than the one which was in question and tested these. The two purest specimens in this laboratory at the time were one of the double tartrate of potassium and sodium which had been recrystallized a large number of times, and one of cane sugar which had been repeatedly recrystallized from alcohol. These two specimens may certainly be regarded as in the strictest sense chemically pure. Both of these substances gave the reaction for nitrogen distinctly. Of all the substances experimented upon, the pure double tartrate seemed to be best adapted to the purpose, and in continuing the experiments I have since always employed this particular pure specimen to furnish the carbon.

The question naturally suggests itself, whence comes the nitrogen in these reactions? I at first suspected the iron by hydrogen, and my suspicions were increased when, on inquiring into the history of the specimen used, I found that it had been made from ferric hydroxide precipitated by ammonia. To be sure the hydroxide had been washed with the greatest care and had afterward of course been ignited in a current of hydrogen, and it did not seem probable that ammonia or any compound of ammonia and iron could be retained; but still, there was the nitrogen, and it appeared at least possible that it was actually contained in the iron. To test this point ferric hydroxide was precipitated from a solution of the pure chloride by means of sodium carbonate and washed out until no test for sodium could be obtained. This precipitate was then divided into two parts, one of which was dried at once, and the other boiled for some hours with a solution of ammonium carbonate and ammonia. The latter was then washed out, no special precautions being taken to remove all the ammonium salts, and afterward dried. Both specimens were separately reduced in a

current of purified and dried hydrogen. *Both gave the test for nitrogen*, and indeed the one from which all ammonium compounds had been carefully excluded seemed to give the test better than the other.

Another specimen of iron by hydrogen which has been in the collection of chemicals of this laboratory for five years, and which does not take fire by contact with the air, failed to give the nitrogen test. This led me to think that possibly the nitrogen is not contained in the iron, but is absorbed from the air, and that the power to absorb nitrogen in this way is connected with the active condition of the iron. Both the specimens above referred to, which in the active condition readily and invariably gave the test for nitrogen, were allowed to stand for a short time in contact with the air and were then again tested. *Neither gave the reaction.* The same experiment was performed with the specimen of iron by hydrogen first used, and which had been preserved under ether. A portion of this was allowed to stand over night exposed to the air and then gave no indication of the presence of nitrogen. These results make it appear extremely probable that the nitrogen detected when active iron is used is really absorbed from the air. But if this is so, then more thorough contact of the heated reagents with the air ought to increase the quantity of cyanide formed. All the experiments thus far mentioned were performed in test tubes, and of course very little air came in contact with the substance at the bottom of the tube. On heating the necessary mixture in a crucible, however, violent combustion of the sodium took place and no reaction for nitrogen was obtained. To prevent this combustion, a mixture of iron by hydrogen, double tartrate of sodium and potassium and metallic sodium was placed in a hard glass tube, and dry hydrogen passed through while gentle heat was applied to drive off water. Then nitrogen was passed slowly over the mixture, while at the same time it was heated to redness. This process was continued for about ten minutes, when, on allowing the tube to cool, the contents were extracted with water, filtered and treated in the usual manner. To my surprise, *a very large precipitate of Prussian blue was formed*, much larger in proportion than in any previous experiment. The result is so striking that the experiment is well adapted to serve the purpose of a lecture experiment, illustrating the formation of cyanogen from the nitrogen of the air. There can be no doubt that the nitrogen

is really absorbed from the air. The quantity of the precipitate obtained in the last experiment was so great as to exclude the supposition that the nitrogen could have been present in the substances used. Then, further, the fact that the active iron, which readily gives the test for nitrogen, does not give the test after it has been exposed to the air and become oxidized, is a clear indication that the active condition of the iron is an important factor in the process and that the nitrogen can not be in combination with the iron. For, if it were, it is difficult to understand how the spontaneous oxidation of the iron could remove it. The heat evolved can scarcely be sufficient to decompose any nitrogen compound present, for the iron is heated to a much higher temperature in the course of its preparation, and the possible nitrogen compound must have been decomposed by this first application of heat.

I have thus far performed no quantitative experiments, and there are obvious difficulties in the way of making these exact. As it is intended soon to continue the experiments, however, an attempt will be made to determine as nearly as possible how much nitrogen can be taken up and combined chemically by given weights of the reagents. Some other points of interest will also be taken up. Thus, in attempting to exclude the air from the vessels in which the reactions took place, hydrogen was used, and the nitrogen test was not obtained. But on testing a nitrogenous substance (hippuric acid) in the same way, very little evidence of nitrogen was obtained. It would, hence, appear that the test can not be applied in an atmosphere of hydrogen, or that the cyanide is decomposed when heated in hydrogen. On the other hand, Marchand¹ has stated that hydrogen does not interfere with the application of the test.

As a result of the experiments described in this paper, it may be stated with confidence that *when iron by hydrogen and certain non-nitrogenous organic substances are heated together with metallic sodium in an atmosphere of nitrogen, a cyanide is readily formed.* The action is, of course, similar to that which takes place in blast-furnaces and which gives rise to the formation of cyanide of potassium. In the latter case, the carbonate of potassium from the burning of the fuel furnishes the potassium. Nitrogen is always present in large quantity, and the iron is constantly passing from the state of oxide to that of the metal.

¹ Journal prak. Chemie, 49, 355.

Marchand some years ago showed¹ that steel when heated with carbon and potassium can take up nitrogen. It had been previously stated by Schafhäütl² that steel always contains nitrogen. The experiments of Marchand made this statement appear improbable though they did not disprove it. Indeed, later a discussion arose in France on the same subject. Fremy claimed that not only is nitrogen always present in steel, but it is the essential element of the steel. This discussion did not at the time lead to a satisfactory conclusion. Quite recently Müller³ has found nitrogen in not inconsiderable quantity in the gases extracted from Bessemer steel by boring, but thus far he has not been able to determine whether the nitrogen is simply enclosed in the pores of the steel or is chemically combined with it.

I have made a number of experiments with Bessemer steel and with other forms of iron, and have obtained results in accordance with those already on record. It seems possible that as regards steel the nitrogen detected may be partly absorbed from the air and partly present in combination with the iron, though it would be difficult to prove the correctness of this supposition.

MAY, 1881.

¹ Loc. cit.

² Ibid. 19, 409.

³ Berichte deutsch. chem. Gesell. 14, 1.

REVIEWS AND REPORTS.

BRIEF REVIEW OF THE MOST IMPORTANT CHANGES IN THE INDUSTRIAL APPLICATIONS OF CHEMISTRY WITHIN THE LAST FEW YEARS.

[Concluded from p. 66.]

MATERIALS EMPLOYED IN WASHING.

Soap.—The consumption in the manufacture of soap of foreign fats, for the most part the product of hot countries, has very greatly increased, palm oil and coconut oil being of first-class importance, while to a less extent mafurra tallow, cotton-seed oil, peanut oil, and other such materials have been applied to this use. Large additional supplies of fat have come to be regularly obtained by extraction with carbon disulphide, and of late still better with light petroleum spirit, from the "marc" of olive pressing, from colza, cotton, and other seed cakes, from bones, slaughter-house refuse, cotton waste, etc., as has been noticed in a previous portion of this report, and these have in great measure fallen into the hands of the soap-boiler. In some respects, however, the most valuable of modern additions to his resources has been the "red oil" or crude oleic acid turned out in great quantity in pressing the solid fatty acids, palmitic and stearic, used in the manufacture of candles. The facility with which this free acid undergoes saponification, in comparison with the corresponding glyceride, is alone sufficient to distinguish it.

The chief feature in the supply of alkali has been the very general introduction of ready-made caustic soda, as contrasted with the old practice of causticizing the carbonate in the soap factory itself immediately before using it.

Of secondary materials introduced, a large proportion represent simply the fraudulent application of ingenuity in debasing the product with useless solid matter, or with water in excessive quantity, while preserving the appearance of good soap. Most of the so called "silicated" soaps, and those with which aluminum hydrate, potato starch and bone gelatine, with or without calcium phosphate, have been blended in quantity, are illustrations of this lowering of the standard of honest manufacture. The use of carnauba wax as the means of enabling soap to take up petroleum, while retaining the property of complete solubility in water, exhibits a curious case of modified behavior in relation to solvents. Some few of the additions made to ordinary soap for special uses have real value, as for instance the glycerine employed in the bland soap, made in great

perfection by Price's Patent Candle Co. for toilet use upon delicate skin, and the carbolic acid soap intended for medical and sanitary applications.

Greater care than was formerly common is given to the neutrality of soaps manufactured for industrial uses, as by bleachers, dyers, etc., avoiding excess either of alkali or of free fatty acid, particularly the former.

In the actual process of soap boiling, heating by means of steam has come more and more into use, replacing the use of open fires. The proposal to bring about saponification under increased pressure in close vessels, though sound in point of general principle, has not been practically applied on account of various inconveniences in detail which it involves. The most novel suggestion, that of Mr. Whitelaw in 1875, to make soap directly from common salt by heating together a neutral fat, excess of common salt, ammonia and water, raising the temperature to about 150°C . in a closed vessel, although it has not established itself in successful practical application, seems deserving of more careful study than apparently it has yet received.

Accessory Materials used in Washing.—In relation to Clark's process for softening water to be used in washing, it has been shown by experiments made upon the large scale that magnesia-hard water, containing magnesium carbonate dissolved by excess of carbonic acid, may be purified by means of calcium hydrate as completely and easily as water which owes its hardness to calcium carbonate. Clear lime-water proved much more satisfactory in producing precipitation than milk of lime, and from three to five hours sufficed for the settling of the precipitate, leaving the water clear.

Amongst alkaline materials adapted to increase the cleansing power of water, either with or without soap, the most useful which have been brought forward are borax and sodium silicate (soluble glass). The former has become generally available since California has furnished such an abundant supply, and borax soap is manufactured with which the salt is already incorporated. Soluble glass has been employed to some extent in the industrial preparation of new textile fabrics.

The addition of gum to the starch jelly used in giving stiffness to washed clothing has long been practiced with a view to improving the gloss of the surface, especially in order to render the appearance of new clothing attractive. There is some reason to believe that dextrine is substituted for natural gum, although such substitution does not seem to have been publicly noticed. If this be not practiced, it would be well that the efficacy of dextrine for this purpose should be tried, since it is obtainable of excellent color and at low price.

As the "blueing" intended to neutralize to the eye any yellowish tint remaining from imperfect washing or bleaching of cloth,

ultramarine and soluble Prussian blue have to a large extent taken the place of the indigo and smalt formerly in general use.

Of materials capable of rendering vegetable fabrics non-inflammable, retarding greatly their combustibility and preventing their ready ignition by contact with flame, sodium tungstate is best known, and has come into practical use upon a moderate scale. Other substances have however been employed with some success, and but recently a premium has been awarded by the French "Société d'Encouragement pour l'Industrie Nationale" for a mixture to be thus applied, consisting of ammonium sulphate 8 parts, ammonium carbonate 2, boracic acid 3, borax 2, and starch 2, to be dissolved in 100 parts of water.

APPENDIX TO WASHING.

Perfumes.—Many new perfumes of natural origin have from time to time been brought into public notice within the last few years, but a large proportion of these fail to establish themselves in permanent use. Among the more interesting and valuable of such materials may be mentioned: Champa or Champaca attur (*Michelia champaca*), from India; Grass oil (*Andropogon ivaracusa*), from India; Khuskhus oil (*Anatherum muricatum*), from India; Ylang-ylang oil (*Artabotrys odoratissima*), from Philippine Isles; Sampaguita attur (*gen. et sp. ?*), from Philippine Isles; Eucalyptus oils (*Eucalyptus*, of several species), from Australia; Myall wood (*Acacia pendula*), from New South Wales; Toronjil oil (*Cedronella Mexicana*), from Mexico; Lignaloës oil (*Amyris lignaloës*), from Mexico; Licoria wood (*Licoria odorata*), from Cayenne.

The chief novelties in regard to methods for the extraction of natural perfumes have been the substitution of paraffine for ordinary bland fats in the process of "*enfleurage*," thus avoiding the disagreeable consequences of the rancidity which the latter suffer sooner or later, and the employment of light petroleum spirit as an energetic solvent, which may readily be gotten rid of by evaporation at very low temperature, after it has served the purpose of extracting the delicate perfumes of such flowers as the violet, tuberose, jasmine, &c., which will not bear the temperature necessary for distillation with water. Other solvents of similar volatile character have been used; one of the last of these which has been proposed is methyl chloride, as made by Camille Vincent from the vinasse of beet-root molasses distillation.

The rapid progress of modern organic chemistry has contributed sundry artificial perfumes, although not in as great number and variety as the artificial dye-stuffs. Amongst the more prominent of such perfumes are "Mirbane essence," or nitrobenzene, simulating, though not perfectly, the odor of bitter almond; the real oil of bitter almonds, or benzoic aldehyde, identical in character and composition with the natural oil, but made from coal-tar toluene;

"Niobe essence," or methyl benzoate, artificially prepared with artificial benzoic acid; oil of winter-green, obtainable on a large scale and cheaply by means of Kolbe's synthetically made salicylic acid; artificial coumarine by Perkins' beautiful synthesis; and vanilline by the equally admirable process worked out by Tiemann and Haarmann.

MATERIALS FOR WRITING, PRINTING, &c.

Paper.—The most remarkable feature in the recent history of the manufacture of paper has been the substitution for rags to an enormous extent of a great variety of crude vegetable fibrous materials. Chief amongst these have been esparto grass¹ or "alfa" (a sedge from Spain and northern Africa), straw, maize leaves (with which excellent results have been obtained at Vienna), and soft wood of various trees. Bamboo² and sugar-cane or sorghum "*bagasse*," although affording coarse fibre, admit of being successfully used, and are obtainable in immense quantity; they have not as yet been actually employed to any great extent. Short, weak fibre, fit mainly to be worked up along with other and better material, has been obtained from pressed beet-root pulp of the sugar factories, cotton-seed hulls, and a great number of other sources.

The employment of these materials, in which the pure vegetable fibre is incrustrated and cemented together by other substances, has demanded the general application of a disintegrating process, consisting in heating with alkaline lye, often under a pressure of 3 or 4 atmospheres in close vessels. The use of the acid sulphite of sodium or calcium instead of caustic soda for this purpose has recently been patented by Mitscherlich, and it is claimed that the substitution produces fibre much superior in length, strength and whiteness to that yielded by the older process, bleaching with chloride of lime being rendered unnecessary or reduced to a minimum.

There have been sundry improvements in pulping engines, in the details of the bleaching process, and in the paper-making machinery proper, but these either involve no changes of radical importance, or belong to the domain of the mechanical engineer rather than the chemist.

In getting rid of the residual chlorine after bleaching, the tendency has for some years been in the direction of using "antichlors" more sparingly, but washing more thoroughly. It is asserted that editions of books issued during the period when sulphites and thiosulphates were most freely employed as antichlors show manifest signs of more rapid deterioration of the paper

¹ As evidence of the eagerness with which any new fibre really fit for paper-makers' use is seized upon, it may be mentioned that England imported of esparto: In 1860, less than 1000 tons; in 1865, more than 50,000 tons; in 1871, 140,000 tons.

² Bamboo fibre has long been used in China, and, to a less extent, in Japan.

than either those of the last few years or those of the period before chlorine bleaching was practiced. The liberation of free sulphur in a state of extreme subdivision from sodium thiosulphate (old hyposulphite) constitutes a special objection to it. It has been proposed to use in preference to these salts a very weak solution of ammonia.

The theory of resin-sizing of paper has been not long since carefully examined by Wurster and Conradin, and the most advantageous conditions studied for precipitating smoothly and in a very fine state of division the free acids of the resin soap by means of aluminum sulphate. The same chemists advocate the precipitation in the pulp of barium sulphate by the reaction of barium chloride on the sodium sulphate formed in the precipitation of the resin soap. The addition of a little glycerine in connection with the sizing has been found to give a special softness and pliability to the paper.

Of special modifications of paper introduced in comparatively recent times, the most valuable is "parchment paper," made by immersion for a short time in sulphuric acid diluted to 59° or 60° B., and kept at a temperature not higher than 10° or 12° C. By using paper from mixed fibres, as of linen and cotton, which are acted upon with unequal rapidity, and by limiting the extent to which the change is allowed to penetrate beneath the surface of thick paper, products combining horny hardness with flexibility in various different degrees are manufactured. The thin, delicate Japanese paper (chiefly from Kodzu, *Broussonetia papyrifera*, and Kuwa, *Morus alba*), intended for transient use in the form of napkins, handkerchiefs, curtains, etc., and the Japanese waterproof paper in imitation of leather, prepared by treatment with successive coats of a drying oil, have both been reproduced in western hands with a fair degree of success, though not as yet upon a very large scale. An "incombustible" paper has lately been described as made in France by mixing 2 parts of paper pulp with 1 part of asbestos, soaking the mass with a solution of alum and common salt, making into paper on the ordinary form of machine, treating the surface with a solution of shellac, passing between rollers and cutting into sheets. It is said that if this paper be written upon with common ink (from nut-galls and copperas), the paper and writing are not destroyed by exposure to fire, *i. e.* doubtless, not so far destroyed as to prevent the possibility of deciphering the writing. At the time of the great Boston fire a few years ago, it was observed that heavily "clayed" paper most resisted destruction, while pencil marks were more generally found legible than those made with ink.

Ink.—The chief novelty in the manufacture of writing ink has been the introduction of various colored inks—particularly violet; to a less extent red, blue and green—prepared with solutions of the coal-tar colors. These have the advantage of flowing freely from the pen and drying quickly, but they are deficient in dura-

bility, being easily destroyed in greater or less degree by light, heat and age. The best is doubtless that made from soluble aniline black, which material can readily be carried about in the dry state and dissolved in a few moments for use, thus representing the most convenient form of "portable ink." The comparatively moderate price at which vanadium compounds can now be had admits of the revival of Berzelius' suggestion of half a century ago, to use as ink the very dark colored fluid obtained by mixing ammonium vanadate solution with infusion of nut galls; the product was highly recommended by him on the score of color, fluidity and indelibility. Amongst somewhat recent modifications of common writing ink from galls and copperas may be mentioned the addition of salicylic acid as a preventative of moulding, and the use of glycerine in copying ink to prevent rapid drying of the writing.

Amongst new materials for the manufacture of printing ink also, the coal-tar colors have played a principal part. Brilliant effects have been cheaply obtained by means of them. The most interesting form in which they have been applied is that of fatty acid compounds of the color bases, readily miscible with linseed oil, and well adapted to the production of inks for chromo-lithography. In the preparation of the higher grades of ordinary black printing ink there has been no more important improvement than the introduction of the very fine lamp-black, so-called "Diamond black," made by the smothered combustion of natural hydrocarbon gas (chiefly methane) in the petroleum region of Ohio. The purity of the carbon so obtained, its extremely fine subdivision, smoothness, and intense jetty black appearance, render it fit for the production of the very best printing and lithographic ink.

As "indelible" ink for marking clothing, carbon inks of the same general character as those used by printers have come largely into use in the United States instead of the nitrate of silver preparations; but the most valuable novelty in this direction has been the "Jetoline" brought forward a few years ago, intended to develop insoluble aniline black upon the cloth to be marked, by writing with a mixture, prepared in small quantity immediately beforehand, of the two liquids furnished, one of these being a solution of an aniline salt and the other one of a vanadium compound, with the necessary amount of potassium chlorate or other oxidizing agent.

Mucilage.—For mucilage to be used in uniting surfaces of paper, the cheap and nearly colorless dextrine of modern manufacture, and "liquid glues" made from gelatine with a small addition of nitric, hydrochloric or acetic acid, or of alum, aluminum sulphate or zinc sulphate, have largely replaced the natural gums. To prevent fermentative change in this, as in so many other organic liquids, salicylic acid has been found to answer a useful purpose. It has been ingeniously proposed to apply the insolubility of chromated gelatine after exposure to light for sealing letter envelopes in such a way that they can only be opened by tearing or cutting the paper.

The part of the envelope to be covered by the flap, and which is not touched by the lips or tongue, is coated with a preparation consisting essentially of acid ammonium chromate, copper and ammonium sulphate, and a little fine white paper fibre, while the inside of the flap is coated with isinglass gelatine dissolved with the aid of acetic acid. When the envelope has been closed, the two prepared surfaces are after a short time united so as to resist the action of cold or hot water, steam, and weak acid or alkaline solutions. The same material, chromated gelatine, has been employed as a varnish to render paper water-proof. In a different direction gelatine has been made available for writing purposes, by converting a mixture of its strong solution with glycerine into the simple and useful tablets which, under various names, such as "hectograph," "polygraph," etc., have been applied to the reproduction in numerous copies of letters and other ordinary writings in aniline ink.

Artists' pigments.—To the list of the fine pigments employed by artists there are frequently made additions, but the number of new and really valuable materials under this head is quite small. Probably the most important for some years have been artificial ultramarine of various tints, Guignet's bright chrome green (chromic oxide,) and cadmium yellow (sulphide of cadmium). The aniline colors, in the form of lakes, have furnished a number of bright effects, but these blend but poorly to delicate mixed tints, and are sadly wanting in permanence on exposure to light. This latter defect constitutes a grave objection to the use of the vivid "iodine scarlet" (mercuric iodide). Uranium yellow (chiefly sodium uranate) has been a little used as an ordinary pigment, but serves mainly the purposes of glass staining and decorating porcelain. Of other colors which have more or less come into use of late years may be noticed cobalt yellow (Fischer's salt—cobalt and potassium nitrite), light or lemon chrome yellow (barium chromate), Indian yellow (Purée—magnesium euxanthate—long known in the East, but of still very uncertain origin), Cassel green (barium manganate), Arnaudon's and Matthieu-Plessy's greens (chromium phosphates), tungsten greens (copper and chromium tungstates), tungsten blue (tungsten pentoxide), tungsten white (barium tungstate), and copper brown (cupric ferro-cyanide). None of these, however, can be considered as additions of first-class importance to the list of well established pigments.

J. W. MALLET.

RECENT PROGRESS IN AGRICULTURAL SCIENCE.

[Continued from Vol. 2, p. 432.]

RESPIRATION.—That plants, like animals, take up oxygen from the air, to exhale it again in combination with carbon and hydrogen, is a fact which has long been known. The reverse process of the reduction of carbonic acid by the green parts of plants is, however, a much more striking and apparently characteristic function of vege-

tation, so that it has come to pass that the first-named process has been comparatively little studied, and the second has not infrequently been called the respiration of plants, thus tending to convey the notion of a fundamental difference between plants and animals as regards their relations to the oxygen of the atmosphere. More recently, however, greater accuracy of nomenclature has prevailed, the absorption of carbonic acid and exhalation of oxygen being designated as assimilation, while the term respiration is applied to the process which is identical in its general character in plants and animals and which is essential to all life, viz. the taking up of oxygen and its use in the organism to oxidize complex substances and liberate the latent energy which they contain.

The clear recognition of the importance of the respiratory function in plants has led to numerous investigations which have disclosed some interesting results. According to the views described in a previous article, the respiration of plants is closely connected with their proteid metastasis and is a function of the protoplasm of the living cells. This view appears *a priori* very probable, since all vital activities are manifested through protoplasm, and is supported by analogy with the respiratory process in animals, where, we believe, the decomposition of matter in the cells of the body is the primary process, while the oxygen which is taken up unites with the products of this decomposition. The observations of Corenwinder also favor this view. He found¹ that respiration, as measured by the amount of carbonic acid given off, was much more active in young parts of plants, rich in protoplasm, than in those older parts in which the proportion of protoplasm was much less. Freyberg² has made similar observations. He executed comparative respiration experiments on land and marsh plants, measuring the amount of oxygen taken up, and found that the former showed a much greater intensity of respiration, while analysis showed them to be also richer in nitrogenous compounds. On this fact, in connection with the greater supply of air to the interior of aquatic plants through their air-ducts, he bases the explanation of the fact that the roots of these plants thrive in a soil nearly or quite destitute of oxygen. Even among land plants the rate of respiration was found to follow pretty closely the percentage of nitrogen in the dry substance.

Internal Respiration.—As just stated, respiration proper is thought to consist in the oxidation of the products resulting from the splitting up of the nitrogenous matters of the protoplasm. This splitting up itself is believed to take place independently of oxygen, and frequently it goes on in the absence of this element. One of the products of this action is usually, if not always, carbonic acid, which under proper conditions is exhaled, and this process is generally called internal respiration. The action of yeast, and especially its so-called "self-fermentation," furnishes a good ex-

¹ Jahresber. Agr. Chem. N. F. 1, 312.

² Landw. Versuchs-Stationen, 23, 62.

ample of internal respiration. The force necessary to sustain the life of the plant is produced solely by the splitting up of the materials of the cell, and not partly by oxidation as is normally the case in the higher plants. Other fungi behave similarly. Müntz,¹ in observations on *Agaricus campestris*, confirmed in the main the results of previous investigators, and showed that this fungus in the presence of oxygen took up this gas and exhaled carbonic acid, while in the absence of oxygen the exhalation of carbonic acid still continued and alcohol was formed in the plant.

A similar process takes place also in the higher plants. Böhm² has found that when green leaves are placed in a limited volume of an indifferent gas in the dark, the volume of the gas increases, carbonic acid being formed in the leaves by internal respiration and excreted. When the same apparatus was exposed to sufficiently strong light, no change in the volume of the gas took place, the carbonic acid being decomposed again as soon as formed, while the oxygen liberated was applied to sustain normal respiration. So too it was found that when green leaves were placed in a mixture of hydrogen and nitrogen containing 6 to 10 per cent. of carbonic acid and exposed to the sunlight, the volume of oxygen given off was greater than that of the carbonic acid assimilated, and that the difference was more marked the longer the apparatus remained in the dark after being put together. This excess of oxygen came from the reduction of the carbonic acid formed by internal respiration. Déhéraïn and Maissan³ have also observed that green leaves continue to excrete carbonic acid in an atmosphere free from oxygen.

In Böhm's experiments leaves of *Juglans regia* were chiefly employed, and these organs were found to be very sensitive to the presence of oxygen, the smallest trace of this gas in the surrounding atmosphere being sufficient to suspend the internal respiration. Further experiments showed that this was not always the case. When green twigs of woody plants were placed in air or oxygen over mercury in the dark, a diminution of the volume of the gas at first took place, which was attributed either to a chemical retention of oxygen by the organic matter of the twig or to a mechanical retention of the carbonic acid formed in respiration. Before, however, all the oxygen was consumed the volume of the gas began to increase, carbonic acid being formed by internal respiration and exhaled. With slender twigs this only took place when all but a trace of the free oxygen had disappeared, but with thicker twigs it began in an atmosphere which still contained several per cent. of oxygen. The cause of this phenomenon is evidently that the air as it diffuses into the twig is gradually robbed of its oxygen, so that the central cells receive none, and thus exhibit internal respiration while the surrounding air still contains a considerable quantity of oxygen.

¹ Jahresber. Agr. Chem. 18-19, 1, 400.

² Liebig's Annalen, 185, 248.

³ Jahresber. Agr. Chem. 16-17, 1, 273.

The internal respiration of such green twigs may also be rendered evident by immersing them in boiled water and exposing them to sunlight, as was done by Böhm. Treated in this way in the dark, they turned brown in two or three days and entered into butyric fermentation, but in direct sunlight they mostly remained fresh for a week or more and evolved considerable gas (sometimes more than their own volume), consisting chiefly of oxygen. This oxygen was evidently derived from the carbonic acid produced by internal respiration.

This evolution of oxygen by green parts of plants under boiled water in sunlight is, as Böhm himself points out, not a new fact. It was observed by De Saussure in experiments on *Cactus opuntia*, but the cause of the phenomenon was quite different in this case. These plants have the power of absorbing their own bulk or even more of carbonic acid in the dark, and when afterwards exposed to the light set free a corresponding amount of oxygen. De Saussure also observed frequently an evolution of carbonic acid by plants placed in oxygen-free media, but considered it a product of decay, holding that no life was possible in the absence of oxygen. It thus appears that Böhm's results of themselves are not new, but differ from the old ones of De Saussure only in the interpretation given them.

It should likewise be mentioned that Ad. Mayer has observed a similar evolution of oxygen by certain *Crassulaceae*, which was due to the reduction of organic acids in the plant, and that he suggests the possibility of a similar interpretation of Böhm's experiments.

Normal Respiration.—Commonly, when we speak of the respiration of plants, we mean the respiration which is sustained by the oxygen of the external air, and this respiration we may designate as normal or external respiration to distinguish it from the internal respiration just spoken of.

Several recent investigations have had it for their object to ascertain the relations of normal respiration to the temperature and to growth. Among the earliest of these is that of v. Wolkoff and Ad. Mayer.¹ They experimented on germinating seeds, chiefly of *Vicia faba* and *Tropaeolum majus*, in an apparatus devised by them, which permitted a very exact measurement of the amount of oxygen taken up from a confined volume of air. Preliminary trials showed that under uniform conditions the respiration remained constant for several hours, and that the pressure of the air in the apparatus and the percentage of oxygen which it contained had, within quite wide limits, scarcely any effect on the rate of the respiration. It was also found that while changes of temperature affected the rate of the respiration, the latter promptly returned to its original amount when the original temperature was restored. Several series of experiments were then made to determine the influence of temperature on respiration. For temperatures ranging

¹ Landw. Jahrb. 3, 481.

from 16° C. to 35° C. the intensity of the respiration (*i. e.* the quantity of oxygen taken up in a unit of time) was found to be directly proportional to the temperature reckoned from the freezing point of water. Above 35° the plants began to suffer from the high temperature, the tips of the stems appearing flaccid and translucent like frozen or boiled tissue. Exactly these parts, now, are the seat of rapid growth and consequently of rapid respiration, and as a natural consequence the intensity of the respiration was found to diminish at these high temperatures. The authors believe, however, that the respiration of the uninjured parts of the plants continued to increase with the temperature, though not so rapidly as below 35°. At any rate, these results indicate that the optimum temperature for the respiration of these plants is quite high, and considerably higher than the optimum temperature for the growth of most plants which have been examined in this respect.

Experiments were also made upon the influence of light on respiration. As is well known, the effect of light on growing plants is to decrease the growth in length. This effect might be explained very plausibly by the supposition that the light increases the oxidation of the substance of the plant and thus diminishes the supply of matter for the formation of new tissue, but these experiments showed very decidedly that sunlight had certainly only a very slight influence, and most probably none at all, upon the rate of respiration.

These two series of carefully conducted experiments are valuable for the facts they have brought to light regarding the relations of respiration to temperature and illumination, but they are even more valuable because they show that while growth and respiration are more or less related processes, they are not so intimately connected that the amount of one can be inferred from that of the other.

Schützenberger and Quinquand, and also Déhérain and Maissan, have likewise observed that the respiration of plants proceeds at the same rate in darkness and in light.¹

Ad. Mayer² has also investigated the respiration of germinating wheat by means of the apparatus devised by him in conjunction with v. Wolkoff. The results were controlled by determinations of the loss of dry matter suffered by the seedlings, it being assumed that the substances destroyed in respiration had the composition of starch. The results obtained in these two ways were fairly accordant. In the later stages of growth, when the plants became too large to be contained in the respiration apparatus, the second method alone was employed.

The wheat used was all from the same crop and of very nearly uniform weight, each grain weighing 0.05 gram. After soaking for a suitable time, it was allowed to germinate in the dark, and the rate of respiration, *i. e.* the amount of oxygen consumed per day, the daily growth in length, and the loss of dry matter were determined.

¹ Jahresber. Agr. Chem. 16-17, 1, 273.

² Landw. Versuchs-Stationen, 18, 245.

Three series of experiments were made, at temperatures of 11.8° , 23.8° , and 34° C. In each case the rate of respiration was found to increase rapidly at first, to reach a maximum after a certain time, and, after remaining nearly constant for a short time, to again decrease as the supply of organic matter from the seed became exhausted. A comparison of the results obtained at different temperatures showed, as was to be expected, that at high temperatures the maximum rate of respiration was higher and was reached more quickly than at low temperatures, while the decrease after the maximum was passed was equally rapid. The same amount of organic matter which was oxidized in 34 days at 11.8° C., was oxidized in about 16 days at 23.8° C., and in 10 days at 34° C.

As regards the relations between respiration and growth (as expressed by the increase in the length of the plumule), it was found in the first two series that the rate of growth corresponded pretty closely with the rate of respiration, though the former reached its maximum a little later than the latter. In the third series only the loss of dry matter was determined, and this was found not to furnish sufficiently accurate data for a similar comparison. An interesting result was reached by comparing the total amount of organic matter oxidized in the three cases with the total amount of growth.

	Days from beginning of experiment.	Loss of dry matter by 4 seedlings.	Length of plumule.	Length of longest root.
I.	34	0.090 gram	222 mm.	49 mm.
II.	16	0.089 "	252 "	111 "
III.	10	0.090 "	147 "	106 "

A direct comparison like this of plants from different series of experiments is somewhat uncertain, and the results are rather irregular. Nevertheless it is evident that the oxidation of the same amount of dry matter produced decidedly less growth of the plumule in the experiment carried on at a temperature decidedly above the optimum for growth. Mayer therefore concludes that at high temperatures part of the organic matter of the plant is oxidized without producing any visible effect on its growth. This result evidently points in the same direction as those already adduced, and shows that growth and respiration are not strictly parallel processes. In another investigation, supplementary to the preceding, Mayer⁸ has shown by means of respiration experiments executed on the same plants, that the intensity of the respiration is directly proportional to the temperature, beginning nearly at 0° C. and increasing regularly up to about 40° C. According to Sachs the temperature of most rapid growth for the wheat plant is about 29° C., so that we have here another proof of the partial independence of growth and respiration.

As noted, Mayer determined the amount of oxygen taken up by his plants. Rischaw⁹ has made experiments similar to Mayer's,

⁸ Landw. Versuchs-Stationen, 19, 340.

but used an apparatus which enabled him to collect and weigh the carbonic acid given off by a large number of plants, and which made it also possible to continue the experiment with the same plants as long as was desirable. His results on wheat fully confirm Mayer's. Experiments on beans gave quite a different result. It was found that for nearly three weeks the rate of respiration remained practically constant, a result which is evidently connected with the large stock of reserve matters contained in these seeds, and which Rischawi explains by supposing that the cotyledons at first respire vigorously, and that as the young plant begins to respire more and more the respiration of the cotyledons becomes gradually less energetic.

Rischawi also utilized this constancy of the respiration of the bean in experiments on respiration in pure oxygen. The receiver of his apparatus was filled with young bean plants and connected with gasometers from which either air or oxygen could be supplied at pleasure. The amount of carbonic acid excreted was determined every hour, the apparatus being filled with air for the first hour, oxygen for the second hour, and so on alternately. These amounts were found to be sensibly equal whether the respiration took place in air or oxygen. The experiments were executed at temperatures ranging from 2° C. to 30° C. with the same result.

In the first of these reports¹ mention was made of experiments by Böhm and by Bert, showing that growth cannot take place in pure oxygen at the ordinary pressure. Böhm found that the amount of oxygen taken up under these circumstances was the same as when the seeds were exposed to atmospheric air, while Bert found it to be less. Rischawi's results evidently confirm Böhm's, while they perhaps give another indication of the non-parallelism between growth and respiration.

H. P. ARMSBY.

NOTES.

Asbestos Stopper for Combustion Tubes.

Some years ago, when working in the laboratory of organic chemistry of Harvard University, I conceived the idea of an asbestos stopper for combustion tubes, which I make as follows: The asbestos is separated into fine threads, moistened with water, twisted into a plug, crowded into the cylinder of an ordinary steel crusher, such as is used to pulverize minerals for analysis, and compressed

¹ This Journal, 2, 342.

by driving the piston of the crusher down upon it with a hammer, or better, by the screw of a vice. The plug is kept under pressure for several hours, then dried within the cylinder upon a sand-bath, pushed out of the cylinder, and after ignition over a blast-lamp is ready for use.

In this condition the plug loses no weight under prolonged ignition, is elastic enough to make a tight joint when fitted to a combustion tube of suitable size, and may be smoothly perforated with an ordinary cork borer.

Besides simplifying the method of organic analysis by permitting the substitution of short metallic tubes for the long glass combustion tubes in ordinary use, asbestos stoppers are very useful for closing bottles which contain substances corrosive to stoppers of rubber or cork.

J. FLEMING WHITE,

NEWPORT, R. I., April 20, 1881.

Laboratory of U. S. Geological Survey.

Action of Ozone on Germs contained in the Air.

E. CHAPPUIS has attempted to show that ozone has the power to destroy the germs which are the cause of fermentation and other similar phenomena. For this purpose dust from the air was collected on cotton stoppers, and some of these exposed to the action of ozone. The ozonized stoppers were then brought in contact with liquid beer yeast, the necessary precautions being taken to prevent the introduction of other material. Even in twenty days no effect was produced in the clear liquid, while the unozonized stoppers caused turbidity even in a few days from the development of certain organisms. Hence ozone kills the germs in the air which can develop in beer yeast. Extended experiments may show whether there exist any relations between the sanitary condition of a place and the amount of ozone in the air, as according to modern views the spread of contagious diseases is caused by germs or low organisms which are transported by the air.—(*Bull. Soc. Chim.* 35, 290.)

The Quinquivalence of Boron.

Not long since, COUNCLER announced the preparation of an oxychloride of boron of the formula BOCl_3 , analogous to the oxychloride of phosphorus. The existence of this compound indicates the quinquivalence of boron. MICHAELIS and BECKER have attempted to make the oxychloride by a simpler method than that employed by COUNCLER. They first passed ozone into the chloride; then they exposed a mixture of oxygen and the chloride in the form of vapor to the action of the silent discharge of a very strong induction coil; and finally they passed electric sparks for a length of time through a mixture of oxygen and boron chloride. They were unable, however, to obtain even a trace of the oxychloride.—(*Ber. deutsch. chem. Gesell.* 14, 914.)

Evaporation without Fusion.

LOTHAR MEYER has repeated the now well-known experiment of Carnelly which seemed to indicate that ice could be heated to a temperature much above 0° without undergoing fusion, and comes to the conclusion that the ice has not really a temperature above 0° . As regards the form of apparatus and the details of the experiment, reference can only be made to the original article.—(*Ber. deutsch. chem. Gesell.* 14, 718.)

On the Absorption of Solar Rays by Atmospheric Ozone.

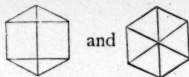
W. N. HARTLEY has been engaged for some time past in studying the absorptive effect produced by ozone on sun light. He has shown that columns of air only three feet in length, containing only $\frac{20}{1000}$ of their volume of ozone, cause a most energetic absorption of the invisible rays, and he has further found that very small quantities of the gas give an azure-blue tint to very considerable volumes of air. He says: "Messrs. Hautefeuille and Chappuis discovered the fact that the ozone possessed a blue color. On filling a glass tube two feet in length for the purpose of some of the preceding experiments, I was surprised to find how small a proportion of ozone is visible to the eye."

"In a column of the atmosphere 1 square centimeter in sectional area, which would weigh 1033.33 grams, the maximum amount of ozone would be at least 0.00258 gram, supposing the gaseous constituents of the atmosphere to form a homogeneous mixture. This calculation is based on the determination of the amount of ozone in the air made by M. Houzeau. The proportion by weight at the *maximum* was $\frac{430000}{1000000}$, or by volume $\frac{700000}{1000000}$. In a 2 foot tube a full pure sky-blue tint is seen when 0.002542 gram of ozone is contained in each square centimeter of sectional area. This number approximates very closely to the above, hence it is evident that if these determinations be correct, the blue tint of the atmosphere must certainly be due to some extent to ozone, at times if not always."

"Now if we consider that 2.5 mgrms. of ozone in each square centimeter of sectional area of a column of air produce a full sky-blue tint, it is impossible to believe that light, which has traversed columns of air under ordinary conditions of temperature and pressure, and 27 to 35 miles in length, has not made its way through 2.5 mgrms. of ozone. The length of an atmospheric column at the ordinary temperature and pressure would be $5\frac{1}{2}$ miles, and while we are in doubt as to the constitution of the higher atmosphere, such reasoning cannot justly be applied to the blue color of the sky."—(*Jour. Chem. Soc., March, 1881, 111.*)

On Carboxytartronic Acid and the Structural Formula of Benzene.

About two years ago, in Barth's laboratory, M. Gruber, by treating protocatechuic acid with nitrous anhydride, obtained an acid of the formula $C_6H_4O_7$, which was called carboxytartronic acid. The acid is tribasic, and hence, according to commonly accepted notions, must consist of three carboxyl and one hydroxyl group united with one carbon atom. Accepting the common benzene formula, it is difficult to explain how an acid of the formula described can be formed from protocatechuic acid without assuming that the carboxyl is not split off, and this assumption seems improbable. BARTH has now succeeded in obtaining the carboxytartronic acid from pyrocatechin, thus proving that the carboxyl of the protocatechuic has nothing to do with the formation first mentioned. The result also makes it appear extremely probable that in benzene four carbon atoms are in combination with each other. As is well known, however, the commonly accepted formula does not represent this condition in benzene, whereas either the prism formula or the "star" is in harmony with the fact recorded by Barth. These formulas may conveniently be represented respectively thus :



It will be remembered that the recent investigations of Thomsen on the thermal phenomena presented by benzene led him to the conviction that one of the above formulas is correct.—(*Monatshefte f. Chemie*, 1, 869.)

On the Conduct of Palladium, Rhodium and Platinum towards Illuminating Gas.

THEODOR WILM has found that, when the double salt of palladium chloride and ammonium chloride is decomposed carefully in a small porcelain crucible over an ordinary Bunsen burner, and the residue ignited after all the ammonium chloride has escaped, the metal turns a copper color and black, while black rings and spots are formed around it, which creep up the inner walls of the crucible, covering it more and more; and, if the crucible be ignited with the cover loosely laid on, there is formed between the cover and the upper edge of the crucible a cauliflower-like growth of carbon. This carbon is not burned up by further ignition even in an open crucible. This phenomenon has nothing to do with the

formation of a compound of palladium and carbon, but consists simply in a decomposition of illuminating gas by the metal and a separation of carbon, which, however, is deposited mostly on the crucible in the neighborhood of the metal, but not on the metal itself. Rhodium conducts itself quite differently. Only a trace of carbon is deposited on the crucible, but the metal itself is markedly changed, a compound with carbon being apparently formed. Platinum conducts itself unlike either of the two metals mentioned. Like palladium it sets free the carbon of illuminating gas by simple contact, but the carbon is then deposited in the pores of the metal and does not enter into combination with it. It appears from these observations that the presence of palladium and rhodium in platinum vessels is objectionable. Platinum crucibles into the composition of which these metals enter soon become blistered or perforated; while vessels of pure platinum do not suffer from long continued use.—(*Ber. deutsch. chem. Gesell.* 14, 874.)

On the Atomic Weight of Platinum.

K. SEUBERT has made a careful determination of the atomic weight of platinum, and finds it to be 194.46. According to the "periodic law" the atomic weight of platinum should be less than that of gold ($\text{Au}=196.2$), whereas hitherto it has been commonly accepted as greater. Platinum now takes that place in the series $\text{Ir} < \text{Pt} < \text{Au}$ which would naturally be accorded to it if its properties be taken into consideration.—(*Annalen der Chemie*, 207, 1.)

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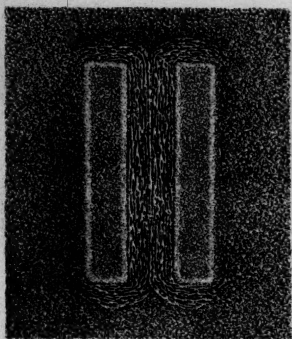


Fig. 1.

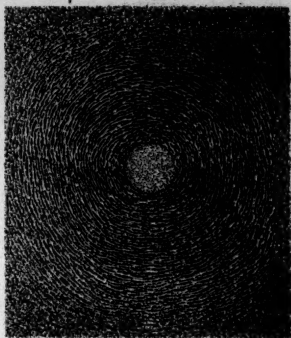


Fig. 4.

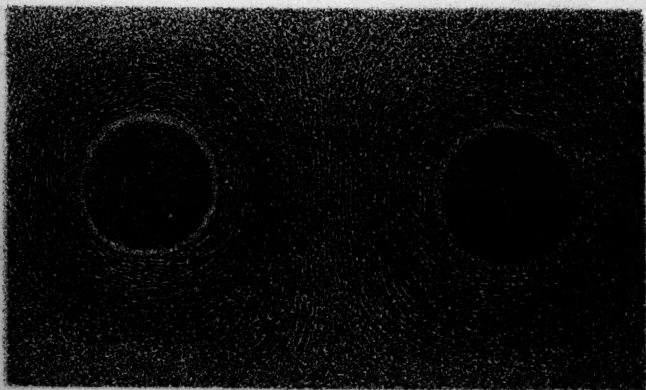


Fig. 2.

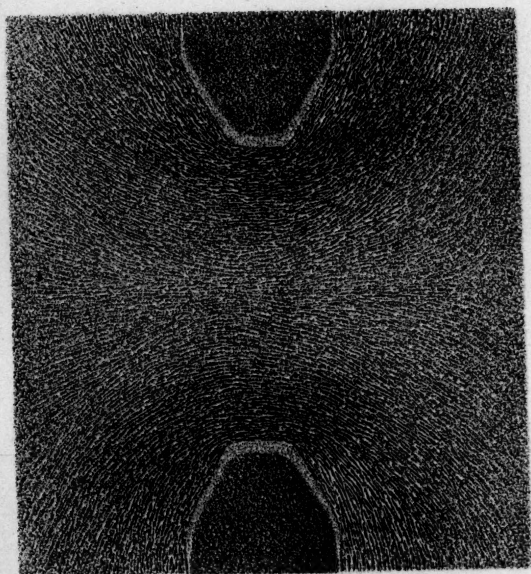


Fig. 3.